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S. W. STRATTON, DIRECTOR

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## A STUDY OF THE DETERIORATION OF NICKEL SPARK-PLUG ELECTRODES IN SERVICE

BY

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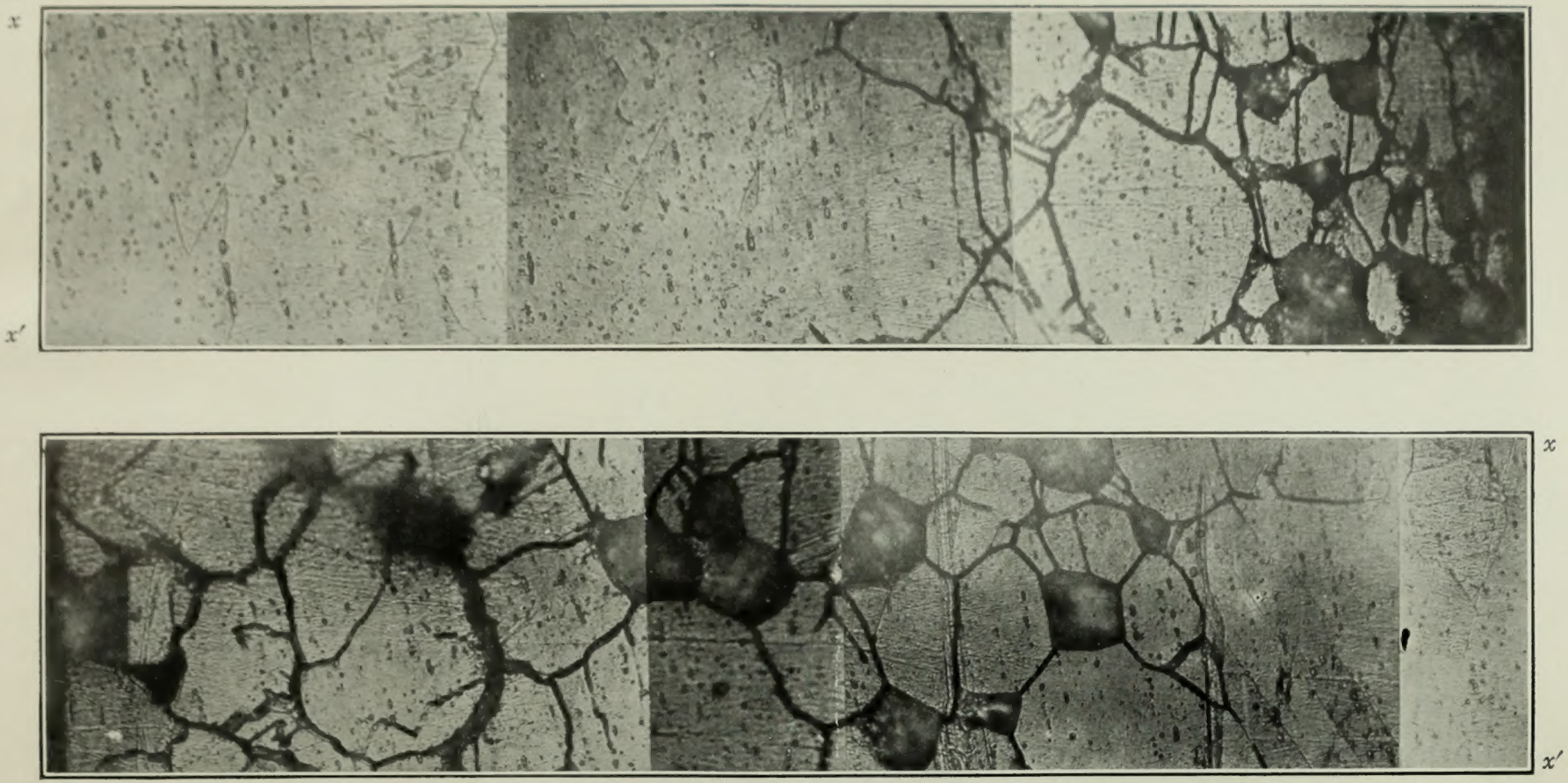


FIG. 1.—(*Frontispiece.*) *Deterioration of nickel electrodes: Medial longitudinal section through a nickel side electrode of a spark plug after deterioration*

The etching develops intercrystalline fissures in the outer layers; some of the crystals have loosened and dropped out of place. Magnification, originally 500 diameters; reduced to 385 in reproduction. Etching, concentrated nitric acid, five seconds

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By Henry S. Rawdon and A. I. Krynitzky

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Character of deterioration of wires during service | 4 |
| 1. Appearance and properties of the changed wire | 4 |
| 2. Chemical composition | 6 |
| 3. Microstructure of commercial nickel wire | 6 |
| 4. Microstructural changes produced during service | 7 |
| III. Possible factors contributing to the deterioration | 9 |
| 1. Chemical composition | 9 |
| 2. Oxidation | 9 |
| 3. Reducing atmosphere | 11 |
| 4. Intense local heating | 12 |
| 5. Influence of combined action of tensional stress and heat | 13 |
| IV. Explanation of service deterioration of electrodes | 15 |
| V. Summary | 16 |


## I. INTRODUCTION

The most commonly used material for electrodes in spark plugs is commercial nickel wire. The relatively high temperature of melting, its excellent heat conductivity, and the slow rate at which the metal is oxidized, even upon continued heating at high temperatures, are the principal determining factors in the choice of nickel for this purpose. The grade of nickel wire commonly used for the electrodes averages 97 per cent nickel, the remainder being manganese, cobalt, iron, and copper, with traces of other impurities always found in commercial nickel.

A peculiar and interesting type of deterioration which occurs in these nickel electrodes during the service life of the spark plug has recently been brought to the attention of the Bureau of Standards. Commercial spark plugs vary greatly in their size and shape, and the electrodes likewise differ considerably as to their relative size, shape, number, and arrangement with respect to each other.

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CORRECTIONS

Table 3, read .09 (for .00)

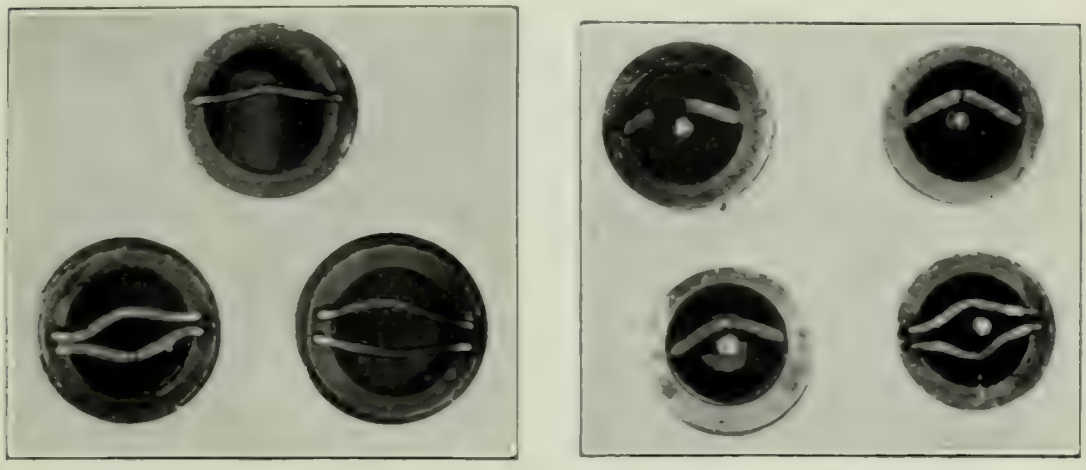
Although this defect was studied in detail in only one of the many varied forms of spark plugs, it became evident from the examination that the deterioration is a characteristic of the material—that is, of nickel wire—rather than of the particular type of spark plug in which it was noted and studied. It appears, however, that the mechanical features of the plugs have a considerable bearing on the time required for the deterioration to become serious. The results of this study of the deterioration of nickel electrodes in service should be of value to the makers of all types of spark plugs in which the electrodes are made of this metal.

## II. CHARACTER OF DETERIORATION OF WIRES DURING SERVICE

### 1. APPEARANCE AND PROPERTIES OF THE CHANGED WIRE

The nickel electrodes in which the deterioration was studied were taken from spark plugs in which the electrodes are arranged as a central one with the ground or side electrode attached firmly at both ends to the shell of the plug. In some of the plugs two side electrodes were used, one on each side of the central one. Although both electrodes were found to have deteriorated to some extent, the attack of the central one was quite negligible as compared to that of the side ones. These latter wires had developed in service transverse cracks which in many cases were as sharp and definite as a knife cut. After a separation occurred, the breach widened by loss of material from the ends of the fractured wires until a gap of as much as 1 cm often resulted. Fig. 2 shows the appearance of some of the side electrodes in different stages of deterioration. In Fig. 3 is shown the appearance of the surface of the side electrodes after removal of the carbonaceous deposit which usually covers them. The surface is roughened by a series of parallel transverse cracks; none of these, however, has penetrated deeply enough to cause a break of the wire. In general, these transverse cracks occur more frequently on the side of the electrode on which most of the "sparking" occurs—that is, the one facing the central electrode—than on the farther side. The central electrode shows no appreciable change other than a slight roughening of the tip.

The appearance of the fracture of the side electrodes is that of very brittle material, there being no elongation and no reduction of cross-sectional area. The face of the fracture itself is rough and crystalline. The mechanical properties of three samples of



a b

FIG. 2.—*Service breaks in nickel electrodes: View, slightly reduced, of the end of spark plugs to show the fracture in the side electrodes; a and b represent two different grades of nickel wire*

FIG. 3.—*Surface changes in nickel electrodes: View of surface of side electrode after considerable service, showing the transverse cracks which develop. Magnification, 5 diameters*

new wire said by the manufacturers to be of the same stock as the failed electrodes were determined with the results shown in Table 1.

**TABLE 1.—Mechanical Properties of Nickel Wire**

| Specimen | Character of wire | Ultimate strength | Elongation in— | |
|---|---|---|---|---|
| | | | 8-inch gage length | 2-inch gage length |
| | | Lbs./in. | Per cent. | Per cent. |
| 1 | Hard-drawn | 110 000 | (a) | (a) |
| 2 | Annealed | 73 000 | 26 | 30 |
| 3 | do | 78 500 | 29 | 31 |
| 4 | do | 65 200 | ..... | 28 |

[a] Not determined; very small.

Specimen 1 was said to be the material from which the failed electrodes of Fig. 2, *a*, were made and resembles it quite closely. (See Table 2.) The electrodes shown in Fig, 2, *b*, which were said to have been made from wire similar to specimens 2 and 3, evidently were made from wire quite similar in composition to specimen 4 (see Table 2), though not necessarily of the same mechanical properties.

Specimen 4 is a sample of annealed nickel wire from the Bureau of Standards stock; this material was used in all the experimental work described later (Sec. III).

The fragments of the deteriorated wire electrodes removed from the spark plugs were found on the whole to be rather ductile and to stand several sharp right-angle bends before breaking. The extreme end portion immediately adjacent to the break, however, was brittle and broke readily when an attempt was made to bend it.

An explanation of the embrittlement of nickel wires used for the winding of an electric furnace has been offered by Carpenter.[1] This assumes the presence within the metal of occluded gas, which is liberated under the combined action of electricity and heat. The wires described by Carpenter separated into a bundle of long thin threads after considerable use of the furnace. The explanation does not answer in the present case, in which the wires are always fractured by a series of transverse cracks.

[1] H. C. H. Carpenter, Collected Researches, 8, National Physical Laboratory, Teddington.

## 2. CHEMICAL COMPOSITION

Both the deteriorated electrodes and samples of unused wires were analyzed chemically. The results are summarized in Table 2.

**TABLE 2.—Chemical Composition of Commercial Nickel Wire**

| Specimen | Nickel | Cobalt | Copper | Silicon | Manganese | Iron |
|---|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| (*a*) Failed wires Fig. 2, a | 97.3 | (*a*) | 0.1 | 0.4 | 1.5 | 0.5 |
| | 97.2 | (*a*) | .1 | .4 | 1.5 | .5 |
| (*b*) Failed wires, Fig. 2, b | 99.0 | (*a*) | .1 | .4 | .05 | .4 |
| | 99.1 | (*a*) | .1 | .4 | .05 | .4 |
| (*c*) 1, Table 1 | 97.1 | 0.7 | .14 | .12 | 1.3 | .6 |
| (*d*) 2, Table 1 | 96.9 | .3 | .09 | .25 | 1.6 | .8 |
| (*e*) 3, Table 1 | 97.1 | .3 | .00 | .18 | 1.5 | .8 |
| (*f*) 4, Table 1 | 98.1 | 1.1 | .18 | .07 | .2 | .3 |

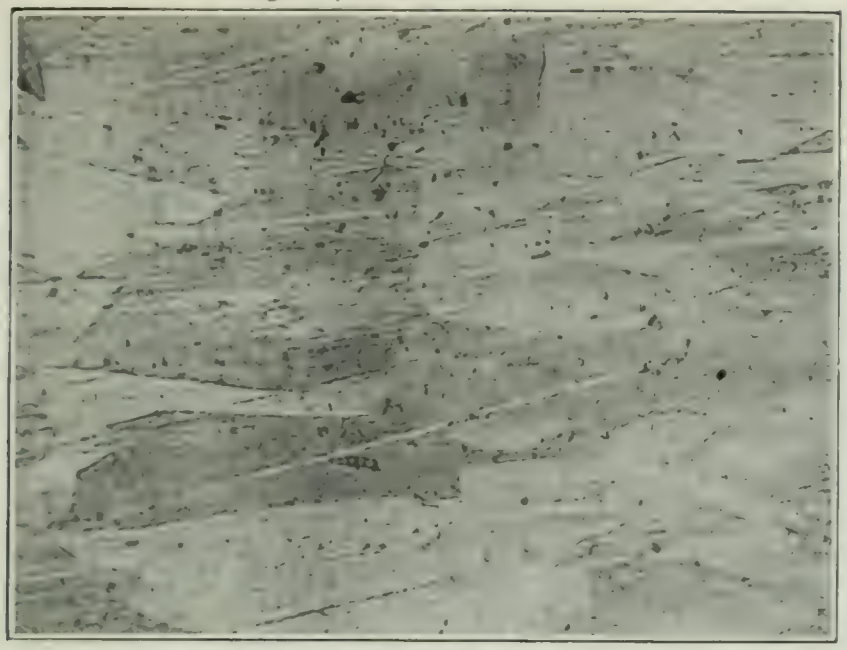
[a] Cobalt was not determined; it is included with nickel.

It will be noted from the results that deterioration occurs in both the usual 97 per cent grade of nickel wire with relatively high manganese content and in the wire of higher nickel content.

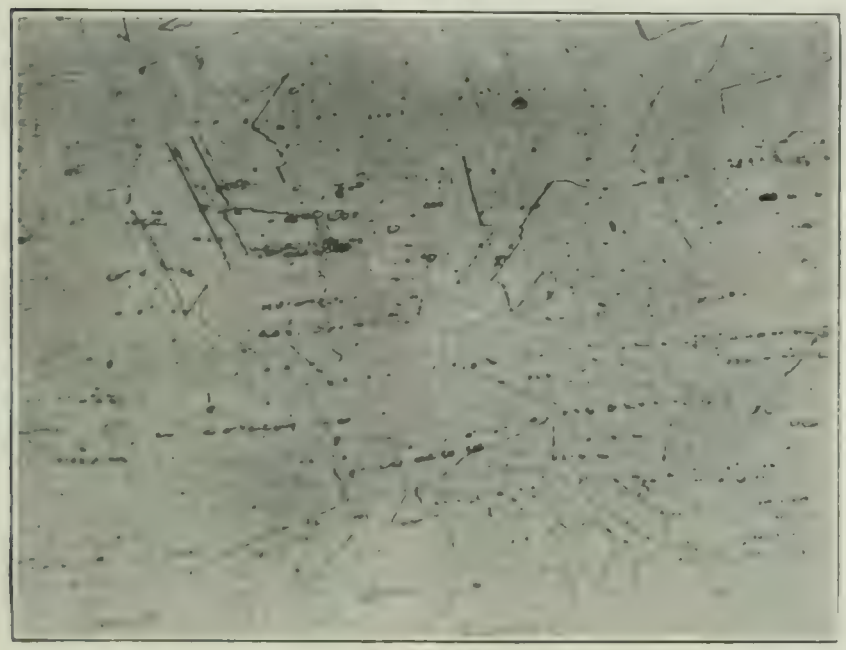
## 3. MICROSTRUCTURE OF COMMERCIAL NICKEL WIRE

In Fig. 4 is shown the microstructure of commercial nickel wire in the hard-drawn and in the annealed state (specimens 1 and 4, respectively, Table 1). The metal consists of but one type of crystals, as is true with pure metals and solid solutions in general. In the hard cold-drawn wire the crystals show the results of the severe distortion due to the drawing by their elongated form; upon annealing sufficiently a recrystallization takes place and the characteristic appearance shown in Fig. 4, *b*, results. The minute inclusions of oxide and other impurities, which have been arranged in lines parallel to the direction of working during the drawing operation, have been dissolved by the strong etching solution (concentrated nitric acid) which is necessary to develop satisfactorily the crystalline structure of nickel. A definite etching pit marking the location of each inclusion results.

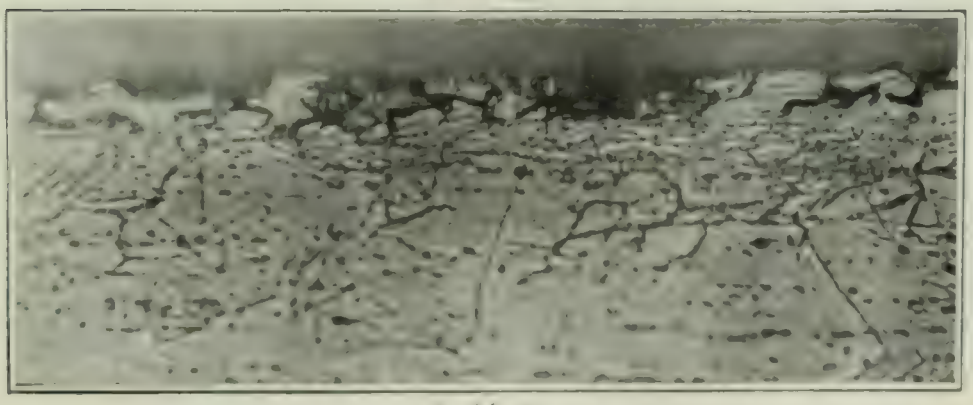
Fig. 4, *c*, shows the outer surface of the annealed nickel wire of Fig. 4, *b*. This wire has received no treatment after the final annealing by the manufacturers. In an extremely thin outer layer a structural change very similar to that which occurs in the nickel electrodes during service has taken place. This undoubtedly occurred during the final annealing; the hard-drawn wires showed



*a* ×435



*b* ×435



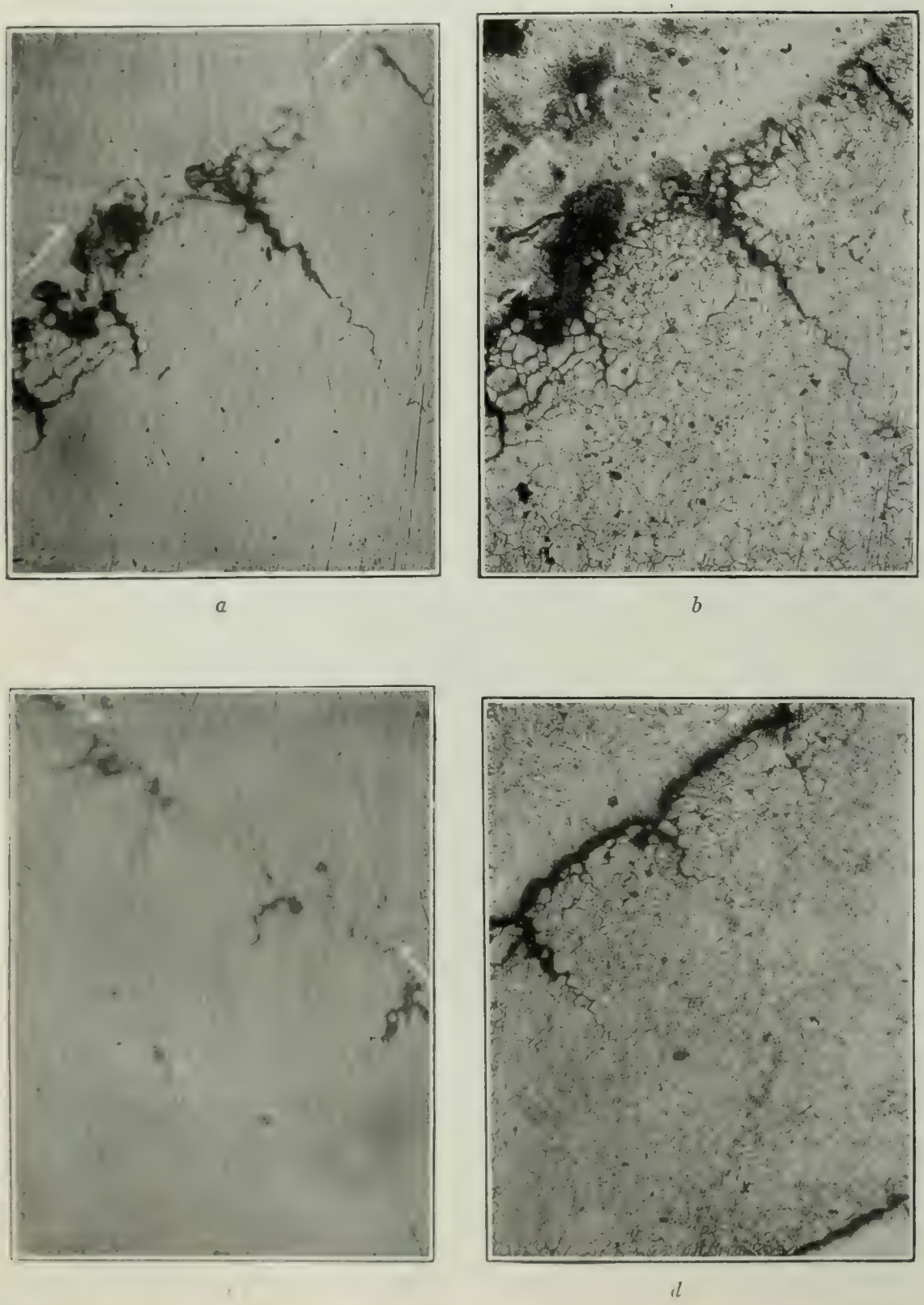
*c* ×417

FIG. 4.—*Commercial nickel wire. Micro-structure of wire of the grade used as spark-plug electrodes*

*a*, Longitudinal section of hard-drawn wire; *b*, longitudinal section of annealed wire; *c*, edge of section shown in *b*, i. e., the surface of the wire.

Intercrystalline fissures appear in a very thin surface layer of metal, these have probably formed during the final annealing of the wire.

Original magnification, 500 diameters; reduced as indicated in reproduction. Etching, concentrated nitric acid, five seconds.

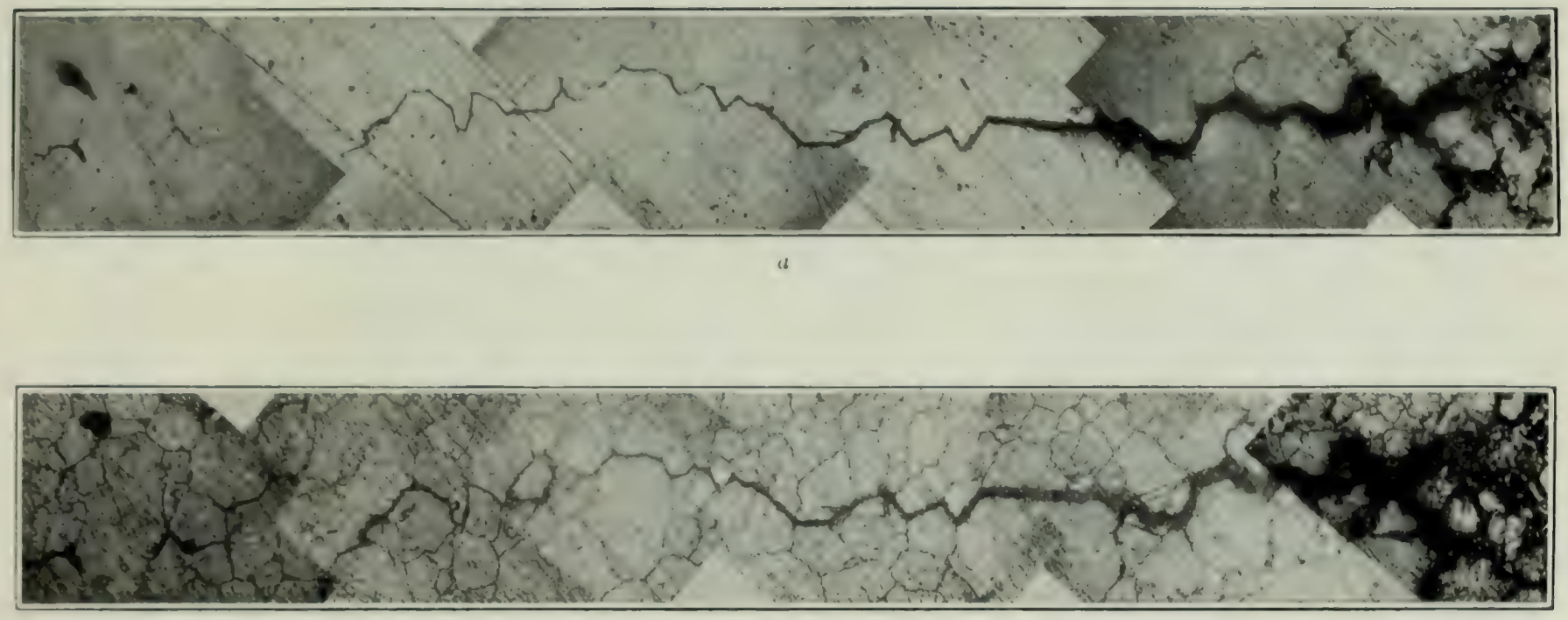


*a* *b*

*d*

FIG. 5.—*Service deterioration of nickel electrodes: Longitudinal sections of side electrodes showing deterioration in service; the arrows indicate the edge of the nickel wire*

*a*, Unetched specimen; *b*, specimen *a* after etching; *c*, unetched specimen; *d*, specimen *c* after etching. Original magnification, 150 diameters, reduced to 72 in reproduction. Etching, concentrated nitric acid, one to two seconds

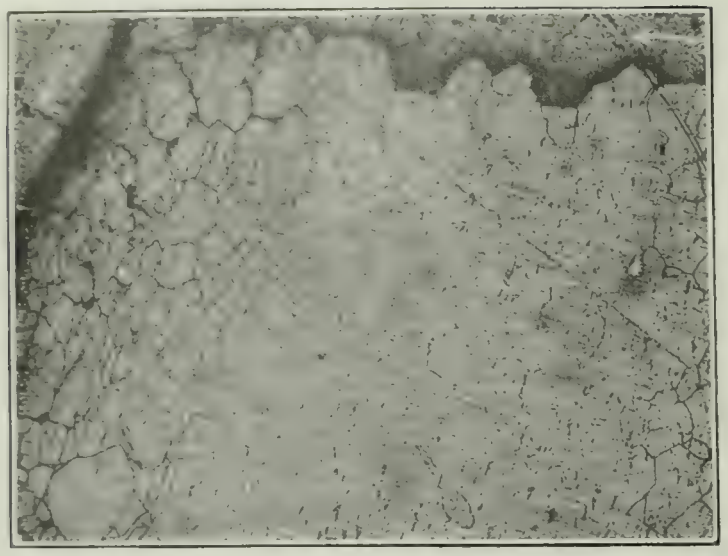


*a*

*b*

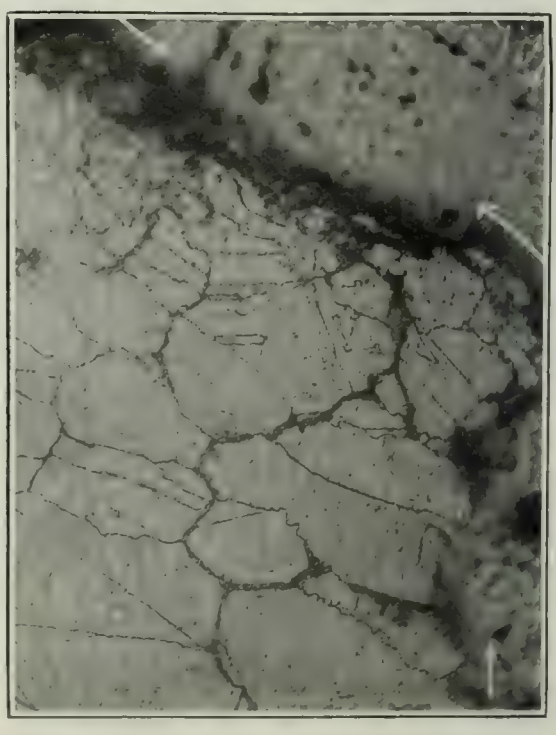
FIG. 6.—*Service deterioration of nickel electrodes: Longitudinal section of a side electrode showing one of the transverse cracks of Fig. 5, d*

*a*, Unetched; *b*, etched, one to two seconds, with concentrated nitric acid
Original magnification, 500 diameters; reduced to 220 diameters in reproduction



*a*

*b*



*c*

FIG. 7.—*Nature of deterioration of nickel electrodes: Longitudinal section through fractured end of wire*

*a*, Section showing the network in the outer zone of the wire and also the intercrystalline fracture. Original magnification, 225 diameters; reduced to 143 in reproduction; *b* and *c* show the lower left-hand corner before and after etching. Original magnification, 225 diameters; reduced to 357 in reproduction. Some of the intercrystalline fissures show a gray nonmetallic substance, evidently oxide. Etching, concentrated nitric acid, one to two seconds

no trace of such a change in the surface metal. In the following discussion (Sec. III) of structural changes produced experimentally in the nickel wire, it should be borne in mind that the extreme surface layer has already been changed to the extent shown in Fig. 4, *c*.

### 4. MICROSTRUCTURAL CHANGES PRODUCED DURING SERVICE

Longitudinal sections of the deteriorated side electrodes were prepared for microscopic examination. The small fragments of the wire were plated with a heavy deposit of electrolytic copper to preserve the edges of the section during the process of polishing; the coated piece was then mounted in a suitable matrix and the resulting composite specimen sectioned and polished. In most of the micrographs a portion of the protective layer of copper appears immediately adjacent to the edge of the section of the nickel wire.

In Fig. 5 is shown the appearance of longitudinal sections of the side electrode. A series of parallel transverse cracks, some of which extend very deeply into the otherwise sound metal, is apparent in the unetched specimen. By etching with concentrated nitric acid for several seconds, the crystal boundaries of the metal are revealed and the intercrystalline nature of the transverse cracks is made evident. Fig. 6, *a* and *b*, shows the course of one of these cracks at a relatively high magnification.

In addition to the intercrystalline transverse cracks which penetrate deeply into the metal, the microscopic examination revealed a zone on the outside of the wire in which the crystal boundaries etch very readily, forming a complete network of intercrystalline fissures; in some cases entire crystals become detached in this zone and fall bodily out of place. These features are shown in Fig. 1, frontispiece, which gives a narrow transverse section entirely across one of the side electrodes.

In Fig. 7, *a*, *b*, and *c*, is shown a portion of one of the side electrodes adjacent to the fracture which occurred in this wire. The break was distinctly intercrystalline, as is to be expected from the nature of the transverse cracks. Before etching, many of the intercrystalline fissures are seen to contain a film of gray nonmetallic substance. This is shown in Fig. 7, *b* and *c*. In Fig. 9 the intercrystalline eutecticlike network, seen in the outer portions of the deteriorated wires, is shown. This appears in the unetched specimen.

Fig. 8 shows a section through the fracture of one of the broken side electrodes and clearly shows the intercrystalline path of the fracture together with some of the sound unchanged metal just back of the face of the break.

The examination of the central electrode showed that a change of the same general character as occurred in side electrodes had taken place in this one, also, but to a slighter degree. In a zone of metal which covers the upper end of the electrode like a cap, the intercrystalline network is well developed. This cap was found in some electrodes to be approximately 0.3 mm (0.012 inch) thick at the tip and to extend as a layer of constantly decreasing thickness for approximately 15 mm (5/8 inch) along the length of the electrode. In the same specimen the side electrode had fractured and a gap of over 7 mm width had formed. In Fig. 10 the general extent of the deterioration of the central electrode is shown. In no case were any of the definite transverse cracks which were noted in the side electrodes found in the central one. Tiny fissures gradually form in the attacked metal which caps the end of the electrode, and groups of crystals become detached, thus gradually shortening the electrode. The relative intensity of the attack in the central and in the side electrodes is shown in Fig. 11. A section of a cross section of the top of a central electrode, the fractured end of a side electrode, and the cool end of the same fragment (that is, the end attached to the shell of the plug) shows the depth of the zone of deterioration in each case.

To illustrate the service behavior of side electrodes anchored at only one end, a number of spark plugs of a different type were examined. These had been used for various periods in a 'Liberty' motor. The side electrodes in this plug are bent at a right angle, fastened to the shell at one end, and terminate near the tip of the central electrode which is of nickel wire of the same size as the side electrodes. Both electrodes in this case show the same type of deterioration as was found in the central electrode of the plugs previously examined; that is, a cap of metal in which the intercrystalline fissures are well developed covers the free end of each. Fig. 12, *a* and *b*, shows the appearance of the two. In none of the electrodes, side or central, were any of the deep transverse cracks found. The plugs had been subjected to a continuous service which varied in the different plugs from 9¾ to 28 hours. The thickness of the zone of deteriorated metal in the electrodes which have had the longest service does not differ

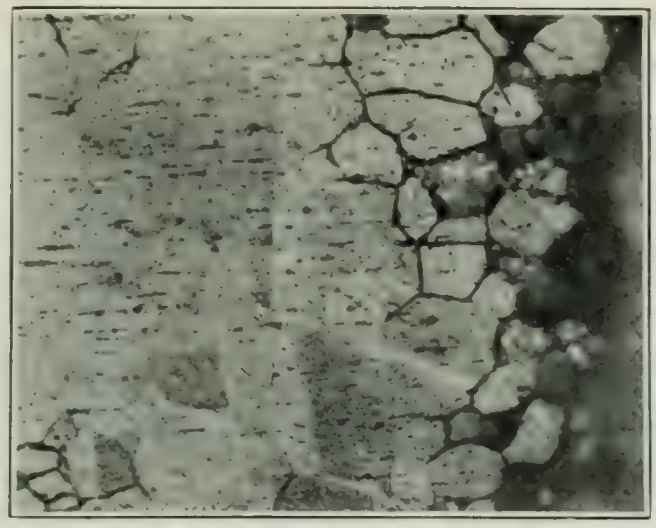


FIG. 8.—*Nature of the fracture of the deteriorated wire: Longitudinal section through the fractured end of a broken electrode*

The path of the fracture is truly intercrystalline; the unchanged sound metal appears just back of the break. Original magnification, 500 diameters; reduced to 263 in reproduction. Etching, concentrated nitric acid, five seconds

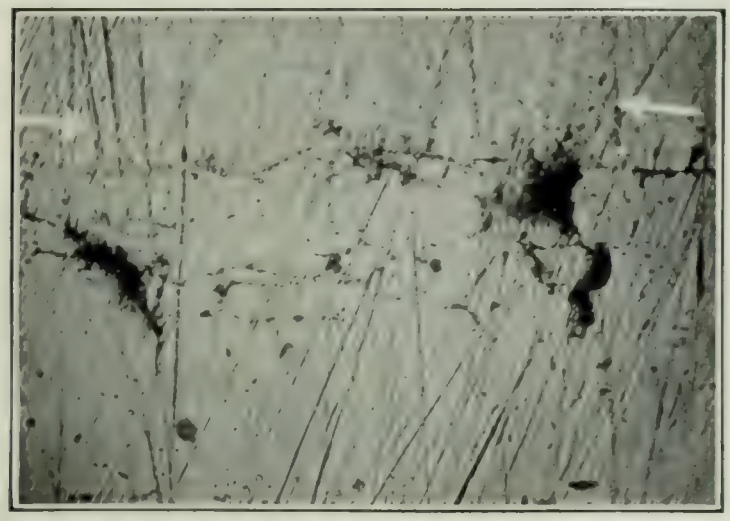


FIG. 9.—*Nature of deterioration: Longitudinal section of a side electrode deteriorated in service, unetched*

A eutecticlike network forms between the crystals in the outer zone of the wire. The arrows indicate the edge of the section of the wire. Magnification, 500 diameters

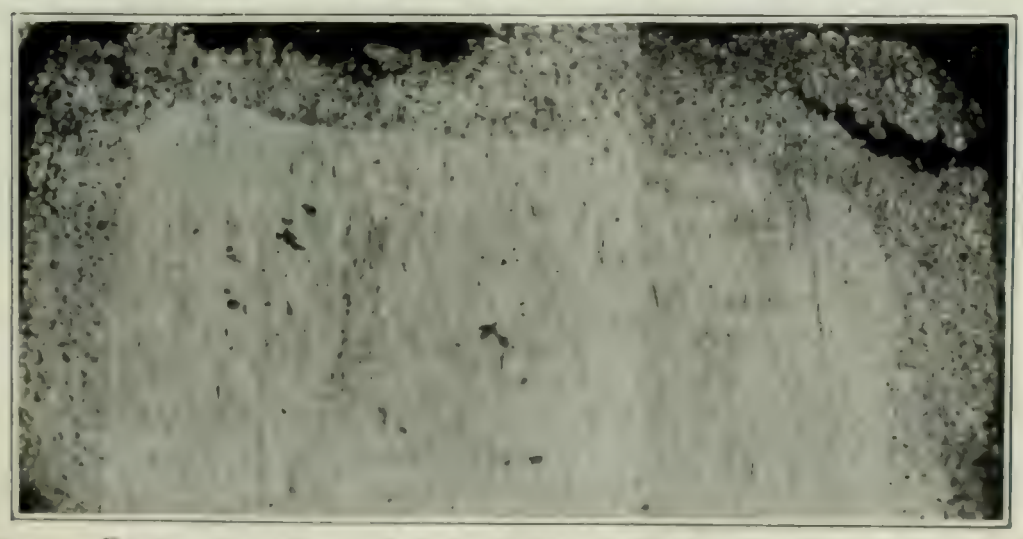
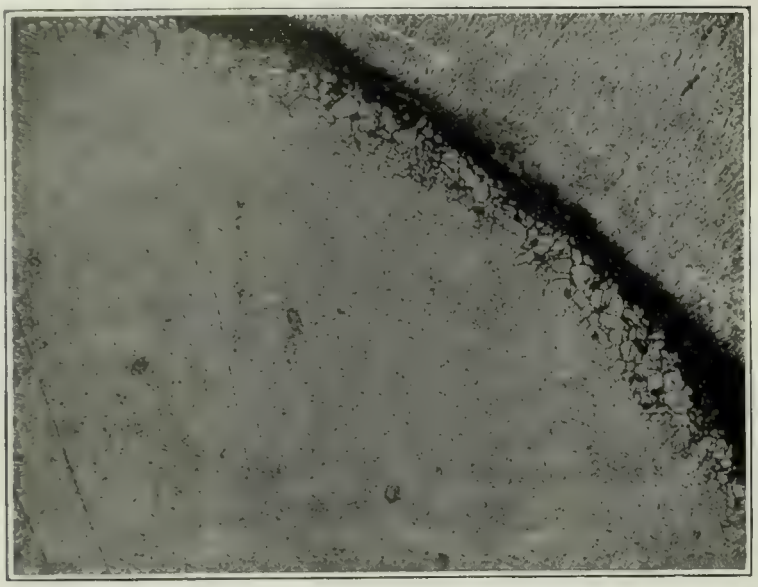


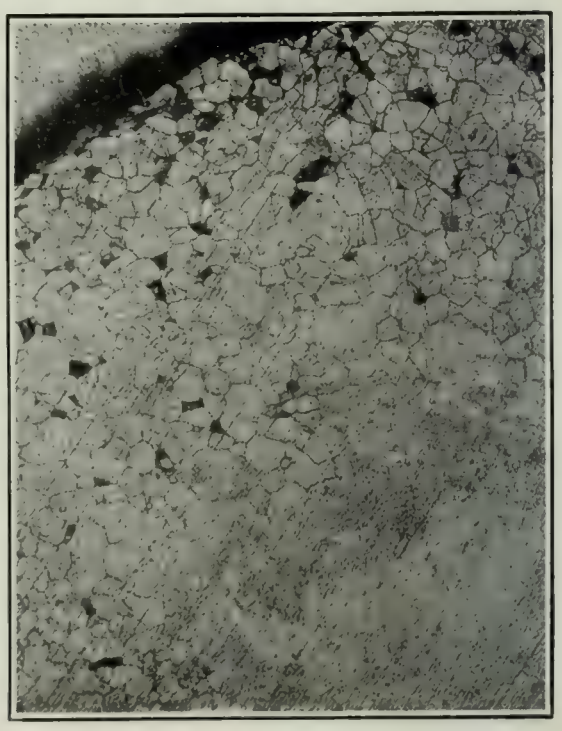
FIG. 10.—*Deterioration of central electrode: Longitudinal section through the tip of the central electrode to show the extent of the deterioration*

A thin layer which entirely caps the upper end has been affected. Original magnification 25 diameters; reduced to 44 in reproduction. Etching, concentrated nitric acid, one to two seconds



*a* ×77

*b* ×72

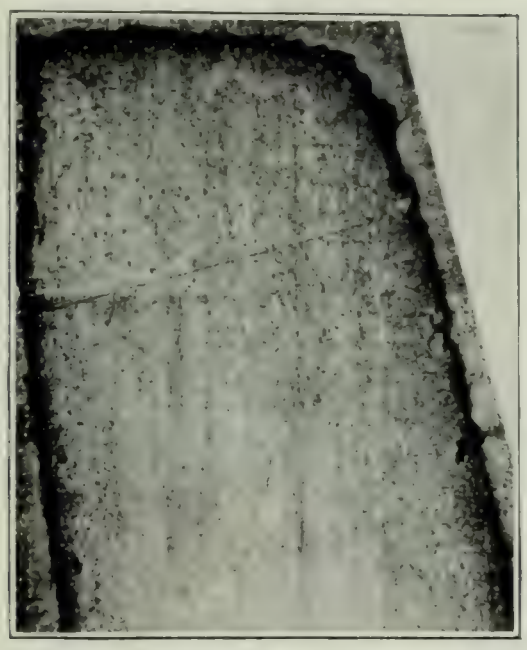


*c* ×72

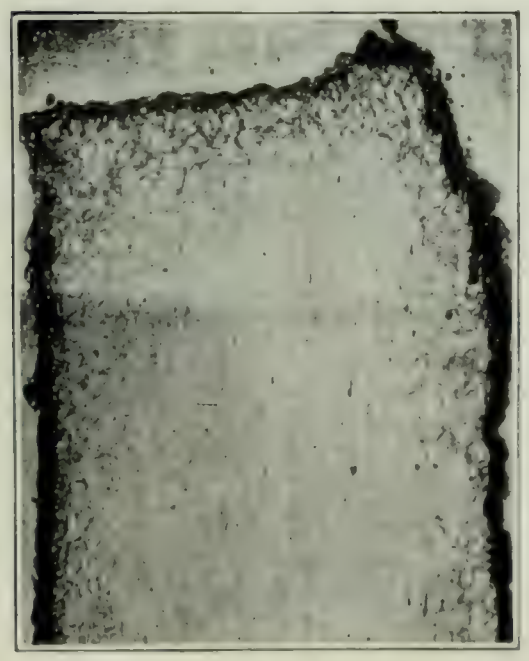
FIG. 11.—*Relative deterioration of central and side electrodes*

*a*, Portion of a cross section of the upper tip of the central electrode; *b*, portion of a cross section just back of the fracture of a side electrode, *c*, portion of a cross section of the opposite end of *b*; that is, where the electrode is attached to the plug shell (cool end)

The center of the ware corresponds quite closely in each case with the lower corner of the micrographs. Original magnification, 100 diameters, reduced as indicated in reproduction



*a*



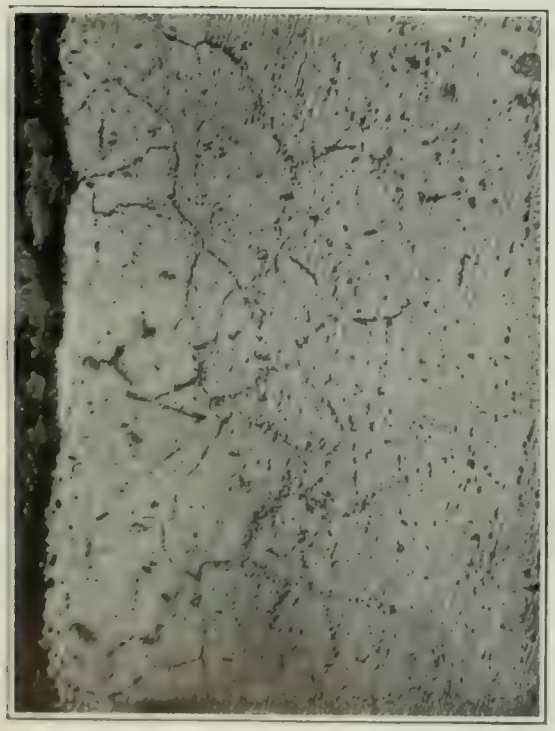
*b*

FIG. 12.—*Electrodes from spark plugs in which the side electrode is anchored at only one end removed after nine hours' service in Liberty motor*

*a*, Longitudinal section of the free (hot) end of the side electrode; *b*, longitudinal section of the tip of the central electrode

Original magnification, 75 diameters; reduced to 44 in reproduction. Etching, concentrated nitric acid, two seconds.

*a*



*b*

*c*

FIG. 14.—*Influence of oxidation upon nickel wires: Longitudinal section of a specimen heated 120 hours, 48 hours at approximately 750° C., 72 hours at approximately 870° C. (Specimen 12, a, Table III.)*

A definite eutecticlike intercrystalline network has formed in the metal just beneath the heavy oxide layer.

*a*, Original magnification, 100 diameters, reduced to 67 in reproduction; *b*, original magnification, 500 diameters, reduced to 335 in reproduction; *c*, original magnification, 1000 diameters, reduced to 735 in reproduction.

The dot work as it first forms is granular in appearance; later a complete film is formed. Etching, concentrated nitric acid, one second.

markedly from that of electrodes of the shorter service. The loss of surface metal from the tip of the wires during service in part explains the rather striking uniformity in thickness of the cap of deteriorated metal.

## III. POSSIBLE FACTORS CONTRIBUTING TO THE DETERIORATION

### 1. CHEMICAL COMPOSITION

From the results of Table 2 it is evident that variations in chemical composition such as occur in commercial nickel wire are not a determining factor in the deterioration of the wire in service. Electrodes of nickel of relatively high purity (for commercial wire) were found to be attacked in the same manner as others of lower nickel content. Wires in which the manganese content was purposely left rather high appear to behave the same in service as those in which the minimum amount of maganese for controlling the sulphur content has been used in the metallurgical operations previous to casting. It was found possible, as described later, experimentally to reproduce the same type of deterioration in nickel wire (specimen (*f*), Table 2) in which the impurities were, in general, less than those of any of the wires which deteriorated in service.

### 2. OXIDATION

In order to determine the part played by oxidation in the development of the intercrystalline network of fissures by which the material is embrittled, several wires (specimen 4, Table 1) were heated at a high temperature for periods of several days. The wires were suspended in a small tube furnace of the resistance type. The ends of the tube were loosely plugged with asbestos to prevent convection air currents, which interfere in maintaining the temperature desired, but no other precautions were taken to exclude the air. (See Table 3, specimens 3*a*, 4*a*, and 12*a*.) In Fig. 13 are shown the structural changes produced by heating for 120 hours, 48 hours at approximately 750° C (740–768° C) and 72 hours at approximately 870° C (862–882° C). A very slight etching (one second in concentrated nitric acid) is necessary properly to show the changes which have occurred. The thick oxide coating which forms has a very smooth shining surface resembling varnish. It is very adherent to the metal beneath. On the inner side of this black oxide layer there is a thin film of

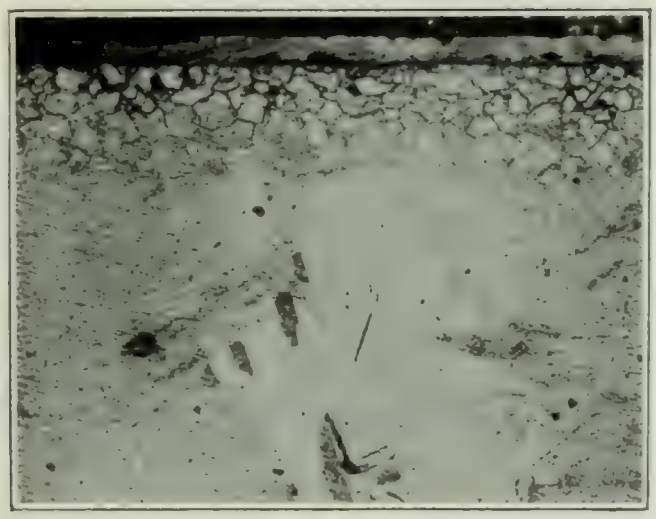
green material. This layer, according to Burgess and Foote,[2] is probably nickelous oxide ($Ni_2O$), the thick outer layer being nickel oxide (NiO). In the outermost portion of the metal of the wire, immediately adjacent to the oxide layer, an intercrystalline eutecticlike network has formed. Microscopic examination at high magnification shows that this network on the inner side (i. e., toward the center of the wire) of the zone in which it has formed consists of discrete particles, probably of the nickelous oxide, which dissolve very readily in the etching fluid, leaving definite etching pits. The appearance of the granular network is that of a eutectic. Without doubt this network indicates the manner in which the oxidation progresses into the solid metal. A similar tendency of steels of a rather high nickel content to oxidize selectively along the boundaries of the crystals has been pointed out by Stead.[3]

A series of heating and cooling curves were taken to illustrate the behavior at high temperatures of nickel which had been oxidized by heating for 120 hours as given above. No evidence was obtained in the behavior of the metal as recorded in the heating and cooling curves that the eutecticlike network fuses within the temperature range, 500 to 900° C, although it is formed at a temperature considerably below the upper limit given. The heating and cooling curves obtained were identical with those of the same material before oxidizing.

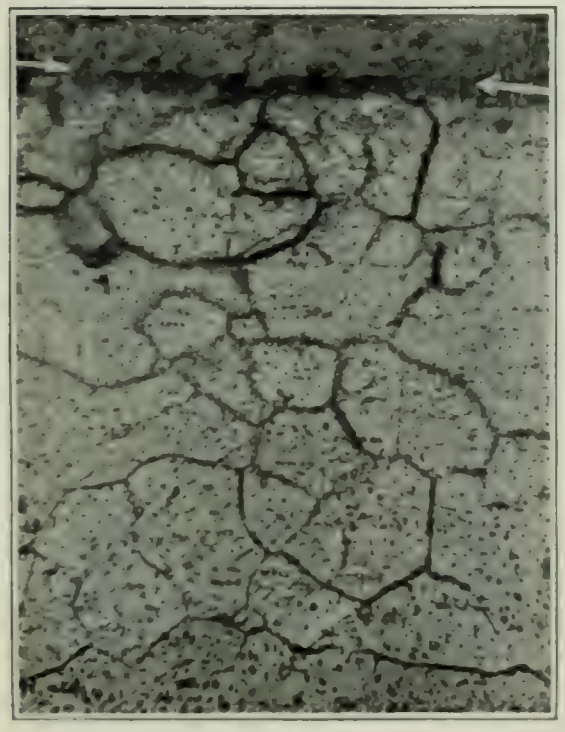
As the oxidation progresses, the isolated particles of the eutectic coalesce, and a continuous film is formed as is to be seen in the outer portion of the zone of the intercrystalline network (Fig. 13b). In Fig. 14 the same material is shown after deeper etching, and the appearance of the structure is identical with that of the electrodes which have deteriorated in service.

Upon long-continued heating, the width of this zone of intercrystalline network widens and a considerable embrittlement of the wire results. Long-continued heating also increases the crystal size of the metal very materially and this adds to the weakness of the overheated metal. In none of the wires which were heated was it possible to produce the definite transverse intercrystalline cracks such as were found in the deteriorated electrodes, and by which the fractures are caused. It would appear that continued heating in the presence of air at a high temperature contributes to the embrittling of the material. The effect of oxida-

[2] C. K. Burgess and P. D. Foote, Bureau of Standards, Scientific Paper No. 224, p. 53.
[3] J. E. Stead, Jour. Iron and Steel Inst., 2, p. 243; 1916.



*a*



*b*

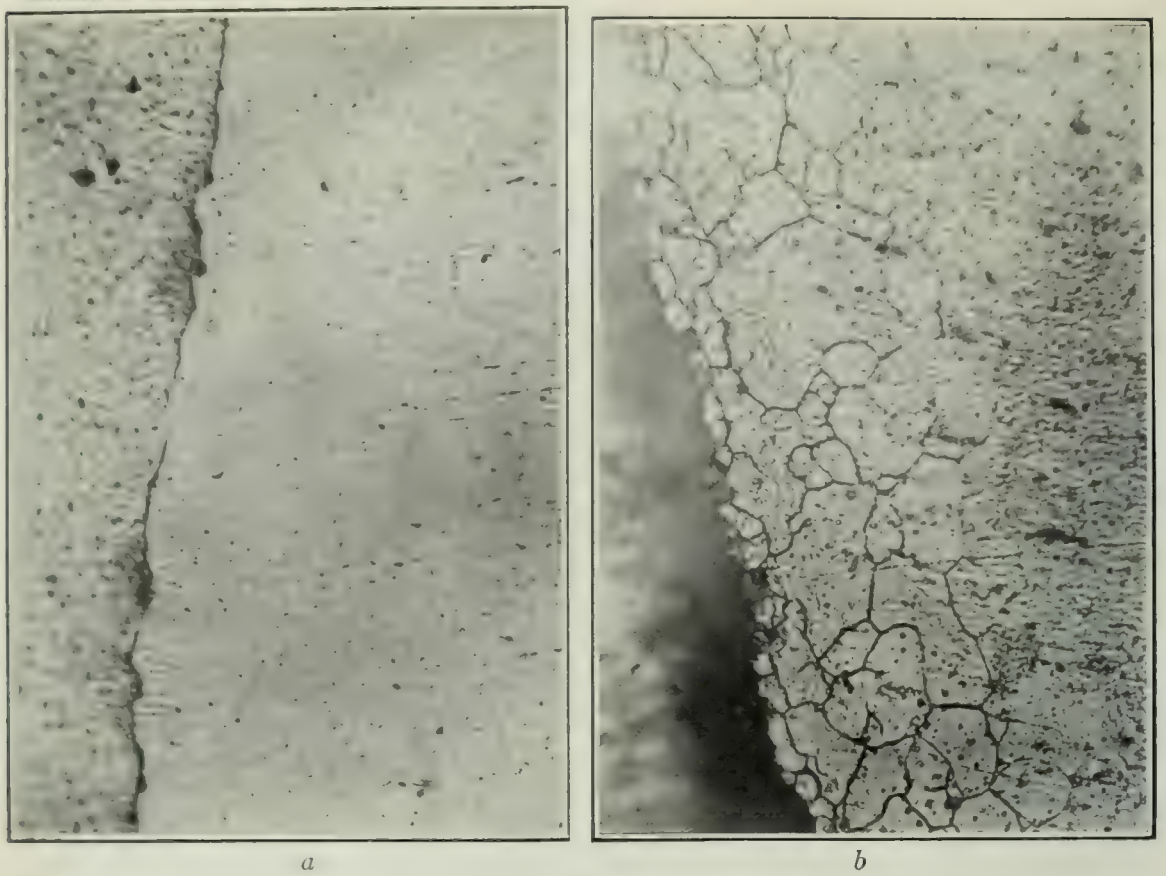
*c*

FIG. 14.—*Effect of oxidation upon nickel wires*

Same material as Fig. 12. Etched deeply

*a*, Original magnification, 120 diameters, reduced to 65 in reproduction; *b*, original magnification, 500 diameters, reduced to 385 in reproduction; *c*, original magnification, 1000 diameters; reduced to 739 in reproduction

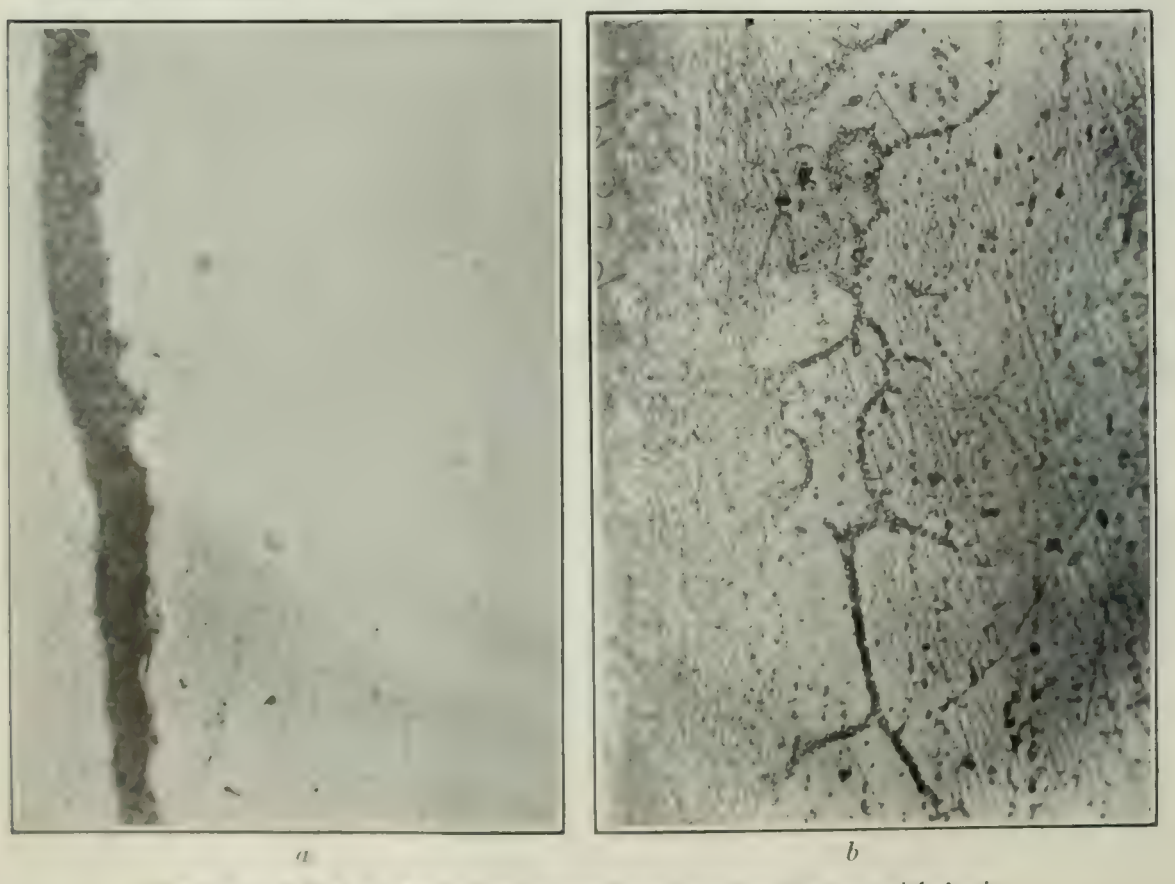
The granular eutecticlike network has dissolved, leaving numerous etching pits at the crystal boundaries. Etching, concentrated nitric acid, eight seconds



*a* *b*

FIG. 15.—*Effect of a reducing atmosphere (carbon monoxide) upon nickel wire*

The wire was heated for five hours in carbon monoxide at 720° C.
*a*, Cross section (unetched) of the heated portion of the wire; *b*, similar cross section; etched, concentrated nitric acid, five seconds
Original magnification, 500 diameters



*a* *b*

FIG. 16.—*Effect of a reducing atmosphere (acetylene) upon nickel wire*

The wire was heated for about three hours at 950° C., the gas was passed over the hot wire intermittently; a heavy deposit of carbon formed
*a*, Cross section of the heated portion of the wire unetched; a thin brittle layer, probably carbide, formed on the surface of the wire; *b*, similar cross section, etched, concentrated nitric acid, five seconds
Original magnification, 500 diameters

tion is very slight, however, compared with that of some of the other possible contributing causes, and may probably be disregarded as one of the causes of the embrittling.

### 3. REDUCING ATMOSPHERE

The effect of a strongly reducing atmosphere upon hot nickel wires was determined by heating wires (specimen 4, Table 1) in carbon monoxide and in acetylene. The carbon monoxide was prepared by the action of concentrated sulphuric acid upon sodium formate, and was passed through soda lime to remove any carbon dioxide which might be present. Carpenter and Smith have shown that carbon dioxide in any appreciable amount will inhibit the carburization of iron by means of carbon monoxide.[4]

The effect of carbon monoxide was determined at two different temperatures; in the first case (710° C) the gas was passed at a very slow rate continuously over the wire which was contained in a long silica tube heated (electrically) at the center. The wire was heated for five hours. In the second case the furnace was maintained at 980° C and the gas was passed intermittently, the furnace being tightly closed at both ends when the gas was not passing. The specimen was exposed to the hot gas for four hours. In both cases carbon dioxide was produced as was shown by the escaping gas as it bubbled through barium hydroxide, but no pronounced deposit of carbon on the wire was produced. The effect of the gas upon the nickel is essentially the same in the two cases. Fig. 15, *a* and *b*, shows the appearance after the treatment. No change was apparent in the unetched state; slight etching reveals a thin surface layer in which the intercrystalline fissures are well developed.

The specimen which was exposed to acetylene was heated at 980° C for approximately three hours. A very heavy deposit of carbon was produced in this case, and it was not possible to pass the gas through continuously. The surface of the wire became coated with a thin black brittle coating which flaked off on slight bending leaving the surface roughened. Undoubtedly this layer is a carbide. Fig. 16, *a* and *b*, shows the change produced in the wire by the hot acetylene. The wires were still ductile after heating, in both cases, and gave no evidence of pronounced brittleness upon bending.

The effect of the hot reducing gases appears to be somewhat greater than that of an oxidizing atmosphere, although the method of attack is the same in each case; that is, intercrystalline. No

[4] H. C. H. Carpenter and C. C. Smith, Reaction Between Carbon Monoxide and Electrolitic Iron, Jour. I. and S. Inst., 98, p. 139; 1918.

indications of localized action which might result in deep transverse cracks in the wire were observed in any of the wires exposed to the reducing gases; the metal is uniformly affected at the exposed surface.

#### 4. INTENSE LOCAL HEATING

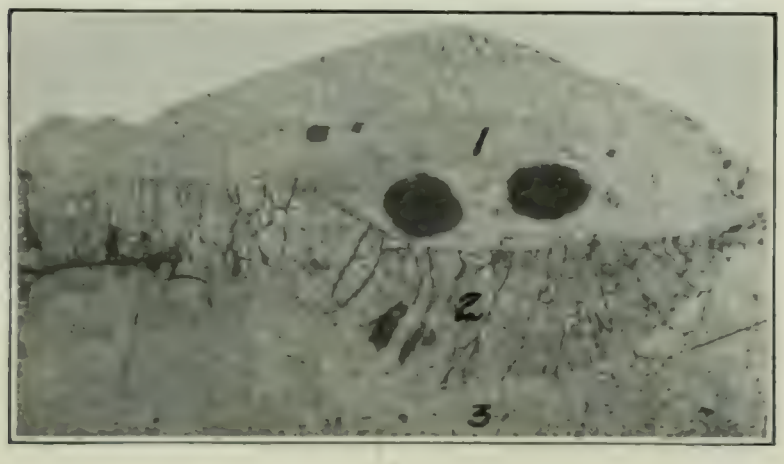
In general, the effect of the electric spark upon the electrode must be regarded as an intense local overheating. Two nickel wires (specimen 4, Table 1) were used as electrodes, and sparks were passed between them. The sparks were produced by breaking the secondary circuit of a transformer (an electric stylograph, used for writing on metals, was used). The current in the secondary winding could be varied from approximately 145 amperes to 400. These conditions, of course, are not comparable with the ignition system of a gas engine. It was not attempted to duplicate service conditions, but rather to accelerate the action. The aim, however, was to heat the metal strongly in a very small area while the remainder remained relatively cool. Specimens were prepared by sparking in air and also in an atmosphere of carbon dioxide, in order that oxidation might be reduced to a minimum. The results obtained in both cases were of the same general character.

In Fig. 17 is shown the appearance of a spot produced by a relatively weak spark. The portion which has been heated strongly is sharply differentiated from the metal which remained rather cool. A network of intercrystalline cracks has broken up the continuity of the overheated metal; these extend for some distance into the surrounding sound metal as intercrystalline fissures.

A much larger overheated area is shown in Fig. 18. This specimen was "sparked" in an atmosphere of carbon dioxide, a much heavier current being used. Three zones are to be noted. An outer one in which the metal was fused, an intermediate one which was strongly overheated and developed the network of intercrystalline fissures, and the inner or relatively cool metal which is unchanged for the most part except for the intercrystalline cracks of the overheated zone which extend into it. The distinct dentritic pattern of the metal in the outer zone is proof that the metal here has solidified from the molten state with the production of this characteristic structural pattern. The line of demarcation between the overheated (but not melted) metal and the relatively cool portion is a very definite one. The intercrystalline cracks have, however, extended into the sound metal of the interior; they are truly intercrystalline in their course.

FIG. 17.—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surface of a nickel wire by means of an electric spark*

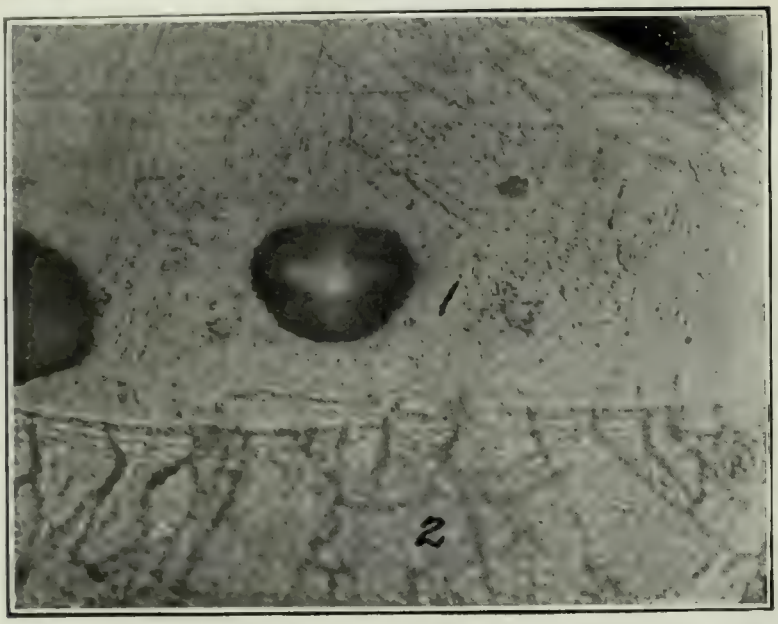
In zone 1, the metal has been highly heated the intercrystalline network has resulted. This network extends into zone 2, the sound metal which has remained relatively cool.
Magnification, 500 diameters. Etching, concentrated nitric acid, three seconds.



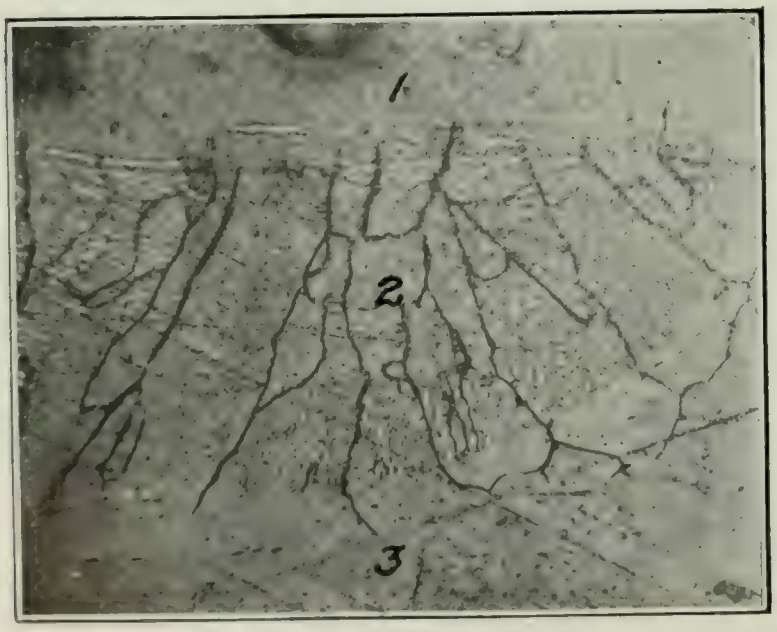

*a*

FIG. 18.—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surface of a nickel wire by the electric spark in an atmosphere of carbon dioxide*

*a*. Magnification, 150 diameters; three distinct zones are seen




*b*




*c*

FIG. 18 (*continued*).—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surface of a nickel wire by the electric spark in an atmosphere of carbon dioxide*

*b*, Magnification, 100 diameters, zone 1 of *a*. The metal has been melted and upon solidification developed the characteristic dendritic structure; *c*, magnification, 500 diameters, zone 2 of *a*. The metal has been highly heated but not melted. The intercrystalline network has been produced; this extends for some distance into zone 3 or 4—the sound metal which remained relatively cool

In none of the wires which were heated by the electric spark could any of the definite transverse cracks be found, although in some cases the effect of as many as 25 to 30 sparks was concentrated in a narrow ring around the wire. The intercrystalline network produced by the local heating by the electric spark properly are to be regarded as a heat effect only, and are not accompanied by oxidation, except in the outermost surface of those produced in air.

### 5. INFLUENCE OF COMBINED ACTION OF TENSIONAL STRESS AND HEAT

In order to explain the formation of the definite transverse cracks which form in the side electrodes, a series of wires (specimen 4, Table 1) were stressed in tension while heated at a high temperature. No attempt was made to reproduce the temperature of the electrode in service since no accurate measurement can be made of the temperature of the small spot at which the spark occurs. The measured temperature of the electrode would be considerably below the actual temperature at this spot. The temperatures used below and elsewhere are considerably above the average temperature of the electrode. The work of Rosenhain and Ewen[5] has shown that the fracture produced in metals which are broken in tension while hot is always intercrystalline in its course. The samples of wire tested were about 2 feet in length; the specimen was inserted through a small vertical tube furnace of the resistance type, firmly attached to a support above and loaded with a weight below. Only the central portion of the wire was heated; in all cases the break took place within this heated portion. The results are summarized in Table 3.

The stress necessary to produce fracture in the hot wire is very small compared with the ultimate strength of the material at ordinary temperatures (approximately 5 per cent). The appearance of the fracture is very characteristic—a sharp crystalline break with no appreciable elongation or reduction of cross-sectional area. A series of small transverse cracks, parallel and close to the face of the break, is usually to be found. Fig. 19 shows the appearance of two of the wires broken in this manner, and shows the characteristic features of the fracture.

[5] W. Rosenhain and D. Ewen, Intercrystalline Cohesion in Metals, Collected Researches, 10 and 11, National Physical Laboratory, Teddington.

**TABLE 3.—Combined Effect of Heat and Stress on Nickel Wires**

[Ultimate strength of wire, 65 000 pounds per square inch; elongation in 2 inches, 28 per cent; diameter of wire, 0.073 inch.]

| Specimen | Average temperature | Load | Result and Remarks |
|---|---|---|---|
| | °C | Lbs./in² | |
| 1 | 942 | 3300 | Wire put in cold furnace; gradually heated; broke in 3 hours. |
| 2 | 970 | 3800 | Put in cold furnace; gradually heated; broke in 3 hours, 50 minutes. |
| 3 | 940 | 3300 | Put into hot furnace; broke in 20 minutes. |
| 3[a] | 940 | No. load. | Heated continuously for 72 hours.[a] |
| 4 | 940 | 3800 | Put into hot furnace; broke in 20 minutes. |
| 4[a] | 940 | No load. | Heated continuously for 72 hours.[a] |
| 5 | 988 | 3800 | Put into hot furnace; broke in 10 minutes. |
| 6 | 993 | 3300 | Put into hot furnace; broke in 13 minutes. |
| 7 | 993 | 3500 | Put into hot furnace; broke in 12 minutes. |
| 8 | 1004 | 3300 | Put into hot furnace; broke in 13 minutes. |
| 9 | 1020 | 3300 | Put into warm furnace; heated rapidly to temperature; wire broke in 30 minutes. |
| 10 | 1100 | 1180 | Wire broke; time not determined as wire broke during night. |
| 11 | 740 | 1180 | Heated 72 hours; wire did not break.[a] |
| 12 | 740<br>880 | 1180 | 48 hours at lower temperature, 72 hours at higher; wire did not break.[a] |
| 12[a] | 740<br>880 | No load. | 48 hours at lower temperature, 72 hours at higher.[a] |

[a] Microexamination showed the beginning of an intercrystalline network in the surface metal.

The changes in the microstructure which are produced by the combined action of tensional stress and heat are shown in Fig. 20. A network of fine intercrystalline fissures with numerous transverse cracks extending into the body of the wire is produced. In Fig. 21 a section through the end of one of the fractured wires is shown. The fracture is distinctly intercrystalline, and has resulted from the formation of transverse intercrystalline cracks which are identical in appearance with those which are found in the electrodes which deteriorated in service.

The brittleness of metals at high temperatures has been explained by Rosenhain and Ewen[6] as due to the weakening of the intercrystalline "amorphous cement" upon heating. The behavior of nickel is very similiar to that of lead, tin, and the other metals of relatively low melting point, which were used in the work of Rosenhain referred to above Nickel differs, however, in one important respect, in that the intercrystalline weakness becomes manifest at temperatures far below the melting point. Metals such as tin, lead, and aluminum must be heated to within a few degrees of the melting point in order to demonstrate this

[6] Loc. cit.

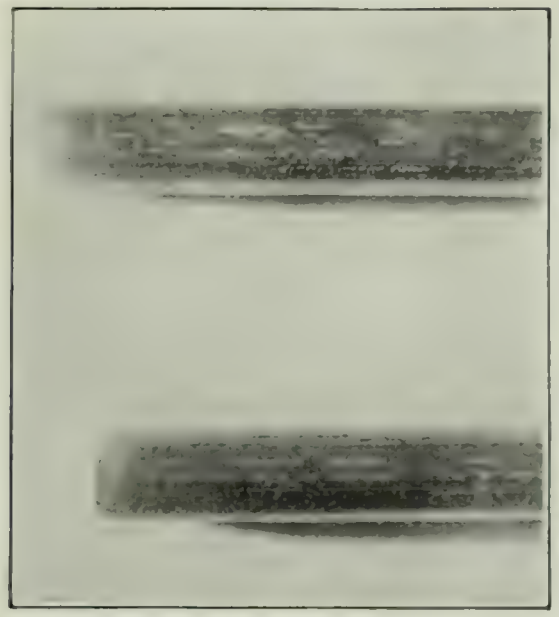
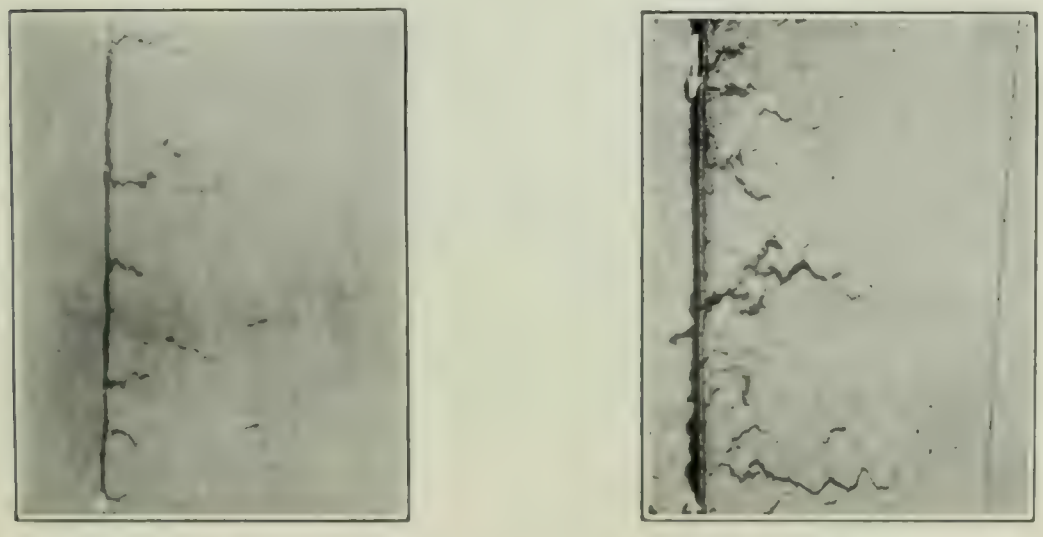


FIG. 19.—*Combined effect of heat and tensional stress upon nickel wires*

Fractured ends of two nickel wires broken in tension while hot. Magnification, 5 diameters



*a* *b*

FIG. 20.—*Combined effect of heat and tensional stress upon nickel wire: Longitudinal section of a nickel wire stressed in tension while hot until fracture occurred. The arrows indicate the edge of the section*

*a*, Unetched; *b*, etched, concentrated nitric acid, three seconds
Original magnification, 100 diameters; reduced to 53 in reproduction

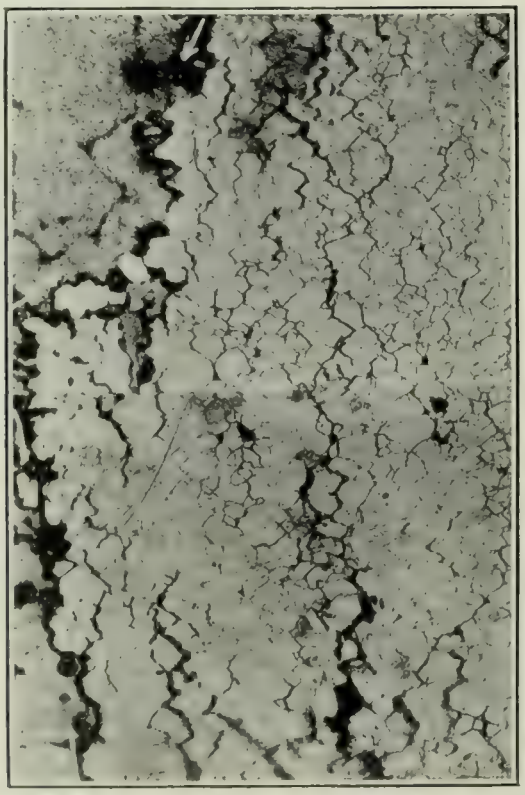


FIG. 21.—*Combined effect of heat and tensional stress upon nickel wire: Longitudinal section through the fracture produced in a hot wire under constant load*

The fracture is distinctly intercrystalline and identical in appearance to those produced in service. The arrows indicate the face of the fracture, the micrograph shows the entire section of the wire. Original magnification, 100 diameters; reduced to 53 in reproduction. Etching, concentrated nitric acid, three seconds

intercrystalline weakness. Nickel also differs markedly from iron in its behavior at high temperatures. Rosenhain and Humphrey [7] demonstrated that iron and mild steel will break under a relatively very low stress at high temperatures with an intercrystalline break but with a very pronounced elongation, often more than 100 per cent. Nickel breaks with no elongation.

## IV. EXPLANATION OF SERVICE DETERIORATION OF ELECTRODES

The types of deterioration of the nickel wires in service as spark-plug electrodes described above are to be attributed to the combined effect of several causes.

The surface layer of wires heated continously in a reducing atmosphere shows evidence of intercrystalline brittleness. This behavior of nickel is in agreement with the fact that deterioration in service begins at the surface and progresses inward. Prolonged heating in the air will, likewise, develop brittleness in the outer layer by the formation of an intercrystalline eutecticlike network. This effect is very slight, however, in comparison with other causes and, probably, does not affect materially the rate of deterioration of the wires. The increased crystal size due to prolonged heating will contribute somewhat to the failure of the wires by facilitating the formation of the transverse intercrystalline fissures.

Local overheating by the electric spark (with the subsequent cooling) gives rise to the definite intercrystalline fissures in such overheated areas which contribute to the local brittleness of the wire. The more rapid wearing away of the metal on the side exposed to the spark, probably, is due to this. The weakening of the "intercrystalline cement" upon heating, and the pronounced intergranular separation which occurs upon application of a very low stress, is, probably, however, responsible for the definite "knife-cut" fractures which occur in some of the electrodes. Such stresses may be due to the effect of unequal heating and cooling of the wire, to the vibratory and explosive action of the spark, and to the constant jarring and vibration of the engine as a whole in service, this being particularly pronounced in the case of airplane motors. The stressing of the side electrodes firmly anchored at both ends by the differential expansion of the shell of the plug is probably, however, the most potent source of danger to which such electrodes are exposed. The other possible stresses cited affect all electrodes, and, probably, aid materially

[7] W. Rosenhain and J. W. C. Humphrey, Collected Researches, II, National Physical Laboratory, Teddington.

in the formation of the intercrystalline network which always is formed and by which the wire is embrittled.

## V. SUMMARY

1. The service deterioration of nickel spark-plug electrodes is shown to be due to an intercrystalline embrittlement of the wire. The cohesion between the grains is so lessened that a network of intercrystalline fissures is formed, and also, under certain conditions, well-defined transverse cracks which extend deeply into the wire.

2. Variation in chemical composition of the nickel wires does not appear to have much bearing on the deterioration; the latter occurs in wire of relatively high purity as well as in the "97-per cent grade" usually specified.

3. Continued heating of nickel wire in the air at a high temperature contributes slightly to the embrittlement of the wire by the formation of an intercrystalline eutecticlike oxide network. This, however, is probably negligible in the deterioration of the electrodes in service.

4. Nickel wires heated in a strongly reducing atmosphere show evidence of an intercrystalline embrittlement of the surface metal. A thin brittle surface skin, apparently carbide, forms in case considerable carbon is deposited upon the wire.

5. Intense local heating by means of the electric spark, together with the sudden cooling, contributes to the embrittling of the wire by the formation of fine intercrystalline fissures in the small overheated zone.

6. The mechanical properties of nickel wire at high temperatures are very different from the properties as ordinarily measured. The application of a relatively low stress to the hot wire is sufficient to fracture the wire by the formation of transverse intercrystalline cracks. The tensional stress due to the differential expansion of the shell and the electrodes is probably sufficient to cause the formation of the transverse breaks in those electrodes which are anchored firmly at both ends. Such cracks were not found in other forms of nickel electrodes.

The chemical analyses of the material were made by J. A. Sherrer, the mechanical tests by R. W. Woodward, and the thermal analysis by H. Scott. Much credit is due J. F. T. Berliner for the very careful work done in the preparation of the sections for metallographic examination.

WASHINGTON, May 23, 1919.

DEPARTMENT OF COMMERCE

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# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 144

# PROPERTIES OF AMERICAN BOND CLAYS AND THEIR USE IN GRAPHITE CRUCIBLES AND GLASS POTS

BY

A. V. BLEININGER, Ceramic Chemist

*Bureau of Standards*

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By A. V. Bleininger

CONTENTS

Part I—PROPERTIES OF AMERICAN BOND CLAYS

Page

I. Introduction ..... 3
II. Methods of testing ..... 4
1. Water of plasticity ..... 4
2. Drying shrinkage ..... 4
3. Slaking ..... 5
4. Modulus of rupture ..... 5
5. Burning behavior ..... 6
III. Results ..... 7
IV. Discussion of individual clays ..... 14
V. Conclusions concerning American bond clays ..... 29

Part II—THE USE OF BOND CLAYS IN THE MAKING OF GRAPHITE CRUCIBLES AND GLASS REFRACTORIES

I. Graphite crucibles ..... 30
1. Graphite ..... 30
2. Artificial graphite ..... 34
3. Crucible mixtures ..... 36
4. Manufacture and use of crucibles ..... 38
II. Glassworks refractories ..... 40
1. Pot mixtures ..... 40
2. Fire shrinkage ..... 42
3. Porosity and refractoriness ..... 44
4. Preheating ..... 45
III. Special pots for optical glass ..... 47
1. Semiporcelain and porcelain pots ..... 47
2. Casting of pots ..... 50
IV. Summary ..... 51

## Part I—PROPERTIES OF AMERICAN BOND CLAYS

### I. INTRODUCTION

Considerable activity has prevailed during the last three years in searching for domestic refractory clays possessing sufficient plasticity, bonding power, and strength to be used in the manufacture of glass refractories, graphite crucibles, and similar products. The properties of the European clays formerly imported

for this purpose have been described in a previous publication.[1] The clay-products section of the Bureau of Standards, during the last two years, has come into possession of a number of samples of American plastic bond clays. It was thought advisable to publish the results of tests made upon clays of this type. The tests made consisted in the determination of the water of plasticity, the drying shrinkage (by volume), the apparent specific gravity in the dried state, the rate of slaking, the modulus of rupture of dried bars made from each clay with and without admixture of sand, the porosity and volume changes at different firing temperatures, and the softening points compared with those of the standard pyrometric cones. From the water content and the drying shrinkage the ratio of pore water to shrinkage water was computed, as well as the percentage of shrinkage water in terms of the true clay volume and the total water content.

## II. METHODS OF TESTING

1. *Water of Plasticity.*—The entire sample was first ground and screened through a 12-mesh sieve, thoroughly mixed, and a sufficiently large portion removed for all the tests. The clay was made up with water and thoroughly wedged till it had assumed what was considered the best plastic condition. It was then made up into briquets 2 by 1¼ by 1 inches and into bars 1 by 1 by 7 inches. The weight of several briquets was determined in the wet state and after complete drying by heating to 110° C. The water of plasticity was taken to be the weight lost in drying, computed in per cent of the dry weight.

2. *Drying Shrinkage.*—In carrying out this determination the volume of the briquets was found by immersing them in kerosene immediately after molding and, after standing for some hours, determining their volume in a volumenometer of the Seger type, provided with a burette, reading to 0.05 cc. After removing the specimens they were allowed to dry, first, at atmospheric temperature and then at 110° C. The dry specimens were weighed at once, again immersed in kerosene, usually for 12 hours or longer, and the volumes were determined as before. From the differences in the volumes of the briquets in the wet and in the dry state the shrinkage was computed in terms of the dry volume. From the weights of the dry specimens and their volumes the apparent specific gravity was readily computed by dividing the volume, expressed in cubic centimeters, into the weight, in grams.

[1] Bureau of Standards Tech. Paper No. 79.

From the wet and dry weights and the wet and dry volumes of the briquets and the true specific gravity of the clay it was possible to calculate the volume of the shrinkage and the pore water in terms of the true-clay volume. These computations were based on the following obvious relations:

$\frac{100s\ (W_1 - W_2)}{W_2} = a =$ volume of total water, in terms of the true-clay volume, expressed in per cent, and

$\frac{100s(v_1 - v_2)}{W_2} = b =$ volume of shrinkage water, in terms of the true-clay volume, expressed in per cent.

In these formulas

$s$ = specific gravity of clay, approaching the value 2.60 quite closely for all clays of this type.

$W_1$ = weight of briquet in the wet state.

$W_2$ = weight of dry briquet.

$v_1$ = volume of briquet in the wet state.

$v_2$ = volume of the briquet in the dry state.

The value $(a - b)$ represents, similarly, the volume of pore water and the ratio $\frac{(a-b)}{b}$ the relation of pore to shrinkage water. By dividing $b$ by $a$ and multiplying by 100 the percentage of shrinkage water, in terms of the volume of total water, may be computed.

3. *Rate of Slaking.*—This was determined by making mixtures of the clays with potters' flint in the proportion of 1:1 and molding into ⅞-inch cubes, which were dried first at atmospheric temperature, and finally at 110° C. Upon immersing the cubes in water at room temperature, suspending them in coarse-mesh baskets, the time of slaking was observed. The more plastic the clay, the longer was it found to resist this action.

4. *Modulus of Rupture.*—The clays in the form of bars 7 by 1 by 1 inches were dried, then heated to 110° C, and upon cooling were broken transversely. From the dimensions of the pieces and the load required to fracture them the modulus of rupture was computed according to the usual formula. According to the quantity of clay available from 10 to 15 such bars were made and tested. Another series of such test specimens was prepared from the mixture of clay and sand in the proportion of 1:1. The sand corresponded to the following sieve analysis:

| | Per cent |
|---|---|
| Residue on 40-mesh sieve | 53.4 |
| Residue on 60-mesh sieve | 35.8 |
| Residue on 80-mesh sieve | 6.9 |
| Through 80-mesh sieve | 3.9 |

All of the sand passed a 30-mesh sieve.

The results given are the averages of at least 10 tests in each case.

5. *Burning Behavior of the Clays.*—The briquets, after thorough drying, were placed in a test kiln, fired with natural gas, and burned at a rate corresponding to a temperature increase of 20° C per hour above 800° C. At temperatures beginning with 1050° C briquets were drawn and cooled slowly by being put in a pot furnace brought to red heat or by being covered with hot sand. When cooled, these specimens were weighed, immersed in water, boiled under diminished pressure for five hours, weighed while suspended in water, and weighed in air while still fully saturated with water. From these data the porosity was calculated by the Purdy formula:

$$\frac{100\,(w\text{-}d)}{(w\text{-}s)} = \text{per cent porosity},$$

where

$w$ = wet weight, in air, of briquet.
$d$ = dry weight.
$s$ = weight suspended in water.

The volumes of the briquets were determined by means of the volumenometer, using kerosene as the displacing liquid. The volume shrinkage or expansion was invariably expressed in terms of the original volume in the dried state.

Both the porosity-temperature and the volume-temperature relations are extremely significant in expressing the burning behavior of the clays. They show at what temperature the state of greatest density (vitrification) is reached, and they also indicate at what point overburning occurs due to the formation of vesicular structure. The volume relations are particularly useful in indicating any expansion which may occur due to the above cause or to the effect of the free quartz which may be present. In general, it may be said that the longer the temperature interval between the point of greatest density (lowest porosity) and the temperature of overburning, and likewise the higher the temperature at which overfiring occurs, the more useful should be the clay as a refractory material.

Clays which reach the state of maximum density only very gradually, owing to their high content of silica, and which never become really vitrified, are also a very useful type, provided they fulfill the other requirements of plastic bond clays. Such materials are particularly valuable for use in glass refractories. For

crucibles, gas-tight muffles, etc., the clays burning dense at a comparatively low temperature, but showing no evidence of overfiring up to quite a high temperature, should be most suitable.

### III. RESULTS

The numerical results obtained in these tests are compiled in Tables 1 and 2. In analyzing the data thus presented it might be advisable to consider briefly the types of clay with which we are dealing here and to establish some arbitrary rules which might aid in classifying the materials. It should be realized that such a classification is necessarily of a tentative character. The clays must be considered from two standpoints, viz, their behavior in the raw state and in burning. From the first point of view two criteria might be employed, the transverse strength of the 1:1 clay-sand mixtures and the ratio of pore to shrinkage water. Arbitrarily we might, perhaps, say that clays showing a modulus of rupture of 325 pounds per square inch or more belong to class A and those between 225 and 325 pounds to class B. The ratio of pore to shrinkage water should in no case exceed 1 for clays of the A type. Further differentiation does not seem possible at the present time. For strong, heavy, plastic clays, low in free silica, the ratio undoubtedly should not exceed 0.75, but siliceous bond clays, such as the Grossalmerode, can not comply with this specification. It might be added that a certain degree of tolerance—say 5 per cent of the values involved—should be allowed in differentiating clays as regards their mechanical strength and the porosity-shrinkage ratio.

With reference to the burning behavior, the overfiring temperature and the softening point are the principal criteria. For very severe service clays of this type should not become decidedly vesicular at a temperature below 1425° C, and should not show a softening point below that of cone 31. It is realized that this specification is not fair to certain plastic clays which are valuable for use in connection with graphite crucibles, especially for brass melting. It seems, however, that even for this purpose the overfiring temperature should not be much below 1400° C and the softening temperature not below that of cone 30. Materials below either of these requirements should not be considered as being high-grade bond clays. Attention might be called to the fact that more weight should be placed on the overfiring temperature than on the softening point. Other conditions being satisfactory, failure of a clay to comply with this requirement within one cone should

not result in its rejection. It is also necessary to note carefully the degree or the rate of overfiring. It is evident that small or gradual changes are not necessarily of importance with reference to the deterioration of the material.

Concerning the general burning behavior of the clays, several classes are to be distinguished in regard to the temperature at which they become dense and that at which overfiring takes place. In this connection it should be said that all clays becoming dense at temperatures below 1400° C should possess a decided range of practically constant porosity. This is especially necessary where the drop in porosity or its equivalent, the rate of shrinkage, is quite rapid. Clays which, upon reaching the state of maximum density, immediately overfire should be ruled out at once, excepting those cases where the overfiring begins at 1425° C or higher. Since these temperatures are already quite high, any overburning at this point is not of serious significance. This is especially true owing to the fact that in all these bodies a certain degree of solution of the refractory grog occurs which will raise the overfiring limit. At the same time the grog content in itself operates against the formation of a vesicular structure. However, we are here concerned with a comparison of the clays. A material overfiring at a high temperature is certainly to be preferred to one reaching this stage at a lower temperature.

Thus, three classes of useful clays are to be distinguished: First, clays burning dense at about 1150° C and showing no evidence of overfiring at 1400° C. This class, provided it possesses the other requisite physical properties, is particularly suited for the manufacture of graphite crucibles used in brass melting. Second, clays burning dense around 1275° C and not overfiring at 1400° C or higher. These clays are adapted for crucibles used in steel melting. When these clays do not overfire before 1425° C, they also become valuable for glass refractories. Third, clays which possess good strength, but do not vitrify at the low temperatures, becoming dense only at 1425° C or higher. These clays, overfiring at about 1450° C or higher, are particularly useful for the purposes of the glass industries. The unsuitable clays are those which become dense anywhere between 1150° C and 1300° C, but possess either no well-defined range between this temperature and that of overfiring or only a short one.

## TABLE 1

| Laboratory No. | Source | Water, in terms of dry weight | Water, in terms of true clay volume | Shrinkage water, in terms of true clay volume | Pore water, in terms of true clay volume | Ratio pore water to shrinkage water | Shrinkage water, in terms volume of total water | Apparent specific gravity of dried clay | Shrinkage by volume, in terms of dry volume | Time of slaking | Modulus of rupture of dried clay | Modulus of rupture of dried mixture of 1 clay: 1 sand | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Per cent | Per cent | Per cent | Per cent | | Per cent | | Per cent | Minutes | Lbs./in.² | Lbs./in.² | |
| 1 | English ball clay | 44.90 | 116.0 | 64.6 | 51.4 | 0.79 | 50.6 | 1.69 | 43.30 | 30 | 376 | 323 | Good plasticity. |
| 2 | Klingenberg, marked A. T. | 39.68 | 104.0 | 66.4 | 37.6 | .57 | 63.8 | 1.79 | 42.58 | 78 | 345 | 381 | Inclined to crack in drying. |
| 3 | New Jersey | 31.23 | 81.9 | 48.3 | 33.6 | .69 | 58.9 | 1.90 | 35.01 | 12 | 475 | 255 | Warps and cracks in drying. |
| 4 | From a St. Louis (Mo.) firm. | 31.14 | 80.7 | 51.5 | 29.2 | .57 | 63.8 | 1.94 | 38.42 | 52 | 838 | 399 | No cracking or warping. |
| 5 | Klingenberg, marked E. T. | 50.66 | 132.3 | 84.8 | 47.5 | .56 | 64.1 | 1.70 | 55.05 | 108 | 230 | 363 | No difficulty in drying. |
| | | | | | | | | | | | | | Sticky and cracks in drying. Specimens checked. |
| 6 | From a St. Louis (Mo.) firm. | 43.63 | 112.0 | 65.1 | 46.9 | .72 | 58.1 | 1.72 | 43.63 | 33 | 328 | 351 | Very fat but dries well. |
| 7 | Kentucky ball clay | 45.28 | 117.6 | 57.2 | 60.4 | 1.05 | 49.6 | 1.55 | 34.53 | 9 | 239 | 234 | Good plasticity; dries well. |
| 8 | Southern Ohio | 22.08 | 58.2 | 32.2 | 26.0 | .80 | 55.3 | 2.01 | 24.46 | 8 | 479 | 281 | Fair plasticity; dries well. |
| 9 | New Jersey plastic clay | 41.85 | 108.8 | 49.4 | 59.4 | 1.20 | 45.4 | 1.56 | 29.86 | 20 | 248 | 185 | Good plasticity; lacking in bonding power; dries well. |
| 10 | English ball clay | 40.33 | 106.5 | 60.8 | 45.7 | .75 | 57.1 | 1.71 | 39.85 | 41 | 366 | 389 | Strong, plastic; dries well. |
| 11 | Southern Ohio | 25.30 | 66.0 | 35.9 | 30.1 | .83 | 54.4 | 1.94 | 27.92 | 8½ | 452 | 309 | Good plasticity; dries well. |
| 12 | New Jersey plastic clay | 34.46 | 89.7 | 35.2 | 54.5 | 1.54 | 39.2 | 1.64 | 22.12 | 5½ | 173 | 94 | Fair plasticity; weak. |
| 13 | Tennessee | 37.65 | 98.2 | 47.8 | 50.4 | 1.05 | 48.6 | 1.66 | 31.01 | 5½ | 187 | 199 | Very good plasticity; dries well. |
| 14 | From a St. Louis (Mo.) firm. | 34.66 | 90.4 | 58.7 | 31.7 | .54 | 62.9 | 1.90 | 42.63 | 117 | 990 | 554 | Excellent plasticity; dries well. |
| 15 | Southern Illinois | 45.16 | 117.4 | 71.0 | 46.4 | .65 | 60.4 | 1.67 | 45.35 | 54 | 439 | 341 | Somewhat "greasy," good plasticity; dries well. |
| 16 | From a St. Louis (Mo.) firm. | 29.54 | ..... | ..... | ..... | ..... | ..... | ..... | 37.02 | 26 | 575 | 351 | Good plasticity; dries well. |
| 17 | Kentucky ball clay | 50.85 | 132.5 | 77.4 | 55.1 | .71 | 58.4 | 1.57 | 46.80 | 36½ | 359 | 362 | Very plastic; warps; excellent bonding power. |
| 18 | Tennessee ball clay | 46.10 | 120.0 | 61.5 | 58.5 | .95 | 51.2 | 1.59 | 37.96 | 18½ | 326 | 228 | Good plasticity; dries well. |
| 19 | Tennessee | 44.73 | 116.3 | 58.9 | 57.4 | .97 | 50.6 | 1.56 | 35.27 | 27 | 387 | 282 | Very plastic; warps somewhat. |
| 20 | Southern Ohio | 26.98 | 68.3 | 39.7 | 28.6 | .72 | 58.1 | 1.91 | 29.21 | 10½ | 482 | 321 | Very plastic; dries well. |
| 21 | Southern Ohio, washed | 26.84 | 69.5 | 37.2 | 32.3 | .87 | 53.5 | 1.88 | 26.98 | 10 | 328 | 277 | Do. |
| 22 | Maryland | 38.91 | 101.0 | 60.5 | 40.5 | .67 | 59.9 | 1.76 | 40.61 | 113½ | 667 | 518 | Sticky; cracks in drying. |
| 23 | Arkansas | 29.02 | 75.3 | 43.7 | 31.6 | .72 | 58.0 | 1.89 | 32.32 | 128 | 817 | 466 | Very plastic and dries well. |
| 24 | Grossalmerode | 20.64 | 53.4 | 26.8 | 26.6 | .99 | 50.1 | 1.99 | 20.57 | 49½ | 502 | 364 | Do. |
| 25 | Southern Illinois | 40.98 | 106.8 | 60.9 | 45.9 | .75 | 57.0 | 1.66 | 38.81 | 45 | 338 | 262 | Somewhat "greasy," but dries well. |
| 26 | Northern Illinois | 19.84 | 51.6 | 27.3 | 24.3 | .89 | 52.8 | 2.03 | 21.08 | 12 | 442 | 240 | Fair plasticity; dries well. |
| 27 | St. Louis district | 25.52 | 66.0 | 37.8 | 28.2 | .74 | 57.2 | 1.95 | 28.52 | 46 | 489 | 263 | Good plasticity and dries well. |
| 28 | Mississippi | 31.39 | 81.6 | 45.0 | 36.6 | .81 | 55.1 | 1.81 | 31.36 | 55 | 645 | 326 | Somewhat sticky and slightly inclined to crack. |

13414°—19——2

**TABLE 2**

| No. | Source | 1050° C | | 1075° C | | 1100° C | | 1125° C | | 1150° C | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage |
| | | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| 1 | English ball clay | 16.64 | 24.80 | 7.30 | 35.52 | 1.99 | 33.84 | 1.62 | 35.30 | 0.19 | 36.72 |
| 2 | Klingenberg, A. T. | 26.15 | 14.80 | 18.62 | ..... | 5.86 | 28.85 | 1.74 | 30.32 | 1.83 | 31.30 |
| 3 | New Jersey | 25.15 | 11.15 | 21.85 | 16.75 | 16.95 | 21.00 | 14.40 | 22.61 | 9.84 | 24.90 |
| 4 | From a St. Louis firm | 23.15 | 6.15 | 21.81 | 9.17 | 17.85 | 11.50 | 18.45 | 12.42 | 15.52 | 13.18 |
| 5 | Klingenberg, E. T. | 23.92 | 23.21 | 6.23 | ..... | 2.90 | ..... | 2.28 | 38.71 | 2.86 | 39.50 |
| 6 | From a St. Louis firm | 33.40 | 14.55 | 30.80 | 17.80 | 22.12 | 25.52 | 10.33 | 32.50 | 8.78 | 33.95 |
| 7 | Kentucky | 37.09 | 11.49 | 33.90 | 16.83 | 26.02 | 26.80 | 21.25 | 30.90 | 17.83 | 34.21 |
| 8 | Southern Ohio | 22.83 | 7.34 | 18.91 | 10.10 | 15.82 | 12.85 | 14.35 | 14.87 | 12.95 | 16.06 |
| 9 | New Jersey | 40.80 | 9.92 | 39.50 | 12.24 | 35.20 | 17.15 | 27.75 | 25.32 | 21.28 | 30.12 |
| 10 | English ball clay | 20.70 | 20.62 | 11.89 | 26.28 | 3.45 | 30.00 | 1.49 | 31.45 | 1.28 | 32.51 |
| 11 | Southern Ohio | 23.55 | 6.66 | 21.72 | 9.97 | 17.61 | 11.95 | 15.01 | 15.61 | 12.05 | 17.95 |
| 12 | New Jersey | 40.40 | 6.13 | 39.20 | 6.76 | 37.90 | 8.68 | 33.90 | 12.86 | 28.38 | 19.30 |
| 13 | Tennessee ball clay | 33.60 | 7.50 | 30.80 | 10.26 | 27.50 | 15.71 | 22.55 | 21.85 | 19.10 | 25.35 |
| 14 | From a St. Louis firm | 24.75 | 7.92 | 21.95 | 9.90 | 18.85 | 13.05 | 16.48 | 15.09 | 11.52 | 17.25 |
| 15 | Southern Illinois | 34.61 | 12.30 | 33.20 | 14.42 | 30.70 | 17.70 | 21.85 | 27.02 | 10.85 | 35.15 |
| 16 | From a St. Louis firm | 24.28 | ..... | 15.88 | ..... | 10.57 | ..... | 7.23 | ..... | 4.89 | ..... |
| 17 | Kentucky ball clay | 37.80 | 13.05 | 30.90 | 22.70 | 22.28 | 30.23 | 18.25 | 33.30 | 16.48 | 33.25 |
| 18 | Tennessee ball clay | 37.50 | 12.84 | 28.70 | 23.45 | 20.75 | 31.14 | 16.95 | 34.72 | 13.90 | 37.10 |
| 19 | Tennessee | 35.48 | 17.90 | 26.55 | 25.60 | 19.03 | 32.20 | 16.50 | 34.82 | 12.71 | 36.55 |
| 20 | Southern Ohio | 22.30 | 8.27 | 18.20 | 13.62 | 15.12 | 16.95 | 14.08 | 18.40 | 11.82 | 20.30 |
| 21 | Southern Ohio, washed | 25.48 | 7.08 | 22.43 | 11.02 | 19.15 | 14.50 | 16.76 | 16.30 | 16.38 | 17.12 |
| | | | | 1090° C | | | | 1120° C | | | |
| 22 | Maryland | ..... | ..... | 21.80 | 18.22 | ..... | ..... | 17.13 | 23.55 | 10.90 | 27.52 |
| 23 | Arkansas | 28.95 | ..... | 28.50 | ..... | 28.00 | .72 | 26.92 | .92 | 26.82 | 2.13 |
| | | | | | | 1090° C | | | | | |
| 24 | Grossalmerode | ..... | ..... | ..... | ..... | 26.06 | 4.14 | 24.92 | 4.97 | 22.52 | 7.59 |
| 25 | Southern Illinois | ..... | ..... | ..... | ..... | 37.30 | 13.50 | 33.90 | 16.12 | 28.89 | 21.60 |
| 26 | Northern Illinois | 23.12 | 7.42 | 22.80 | 7.78 | 20.86 | 10.00 | 18.95 | 11.60 | 16.37 | 14.11 |
| 27 | St. Louis district | 24.90 | 8.70 | 23.35 | 10.34 | 21.10 | 13.62 | 19.75 | 16.19 | 17.05 | 19.30 |
| 28 | Mississippi | 30.32 | 9.75 | 29.80 | 9.90 | 25.30 | 14.15 | 20.80 | 18.62 | 15.96 | 22.80 |

TABLE 2—Continued

| No. | Source | 1175° C | | 1200° C | | 1230° C | | 1260° C | | 1290° C | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage |
| | | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| 1 | English ball clay | 0.31 | 36.90 | 0.68 | 36.63 | 0.69 | 36.52 | 0.50 | 36.60 | 0.77 | 35.91 |
| 2 | Klingenberg, A. T. | 2.50 | 31.71 | 1.54 | 32.65 | 1.36 | ..... | .72 | 33.18 | 1.04 | ..... |
| 3 | New Jersey | 5.80 | 26.95 | 1.83 | 27.28 | 2.83 | 25.05 | 5.66 | 19.95 | 11.01 | 16.78 |
| 4 | From a St. Louis firm | 13.32 | 13.88 | 11.95 | 15.46 | 9.45 | 17.82 | 7.38 | 19.33 | 2.66 | 20.30 |
| 5 | Klingenberg, E. T. | 2.76 | ..... | ..... | ..... | 3.35 | 38.60 | 3.94 | 39.70 | 2.96 | ..... |
| 6 | From a St. Louis firm | 3.95 | 35.50 | 1.23 | 36.45 | 2.00 | 37.92 | 2.44 | 38.60 | 1.76 | 39.30 |
| 7 | Kentucky | 17.05 | 35.40 | 12.95 | 37.01 | 6.13 | 39.00 | .19 | 41.20 | .81 | 41.75 |
| 8 | Southern Ohio | 12.02 | 17.15 | 11.56 | 17.10 | 8.66 | 17.38 | 8.71 | 17.80 | 6.82 | 18.06 |
| 9 | New Jersey | 20.35 | ..... | 16.45 | 33.50 | 14.09 | 35.60 | 11.46 | 38.08 | 8.50 | 38.50 |
| 10 | English ball clay | 1.43 | 33.80 | .92 | 32.80 | 1.11 | 33.10 | .97 | 32.05 | ..... | 31.10 |
| 11 | Southern Ohio | 10.26 | 18.21 | 9.71 | 19.78 | 6.90 | 20.83 | 3.14 | 21.69 | .49 | 21.80 |
| 12 | New Jersey | 27.69 | 20.89 | 27.10 | 22.08 | 22.30 | 25.40 | 19.95 | 28.00 | 16.56 | 29.55 |
| 13 | Tennessee ball clay | 12.65 | 28.95 | 8.13 | 31.42 | 4.04 | 32.70 | .71 | 34.41 | .34 | 35.10 |
| 14 | From a St. Louis firm | 2.12 | 18.27 | 1.02 | 18.96 | 1.12 | 19.56 | 2.75 | 18.87 | 2.82 | 12.15 |
| 15 | Southern Illinois | 6.71 | 34.80 | 3.85 | 35.50 | 2.11 | 35.85 | 2.34 | 38.90 | 2.02 | 38.85 |
| 16 | From a St. Louis firm | 1.91 | ..... | 1.39 | ..... | 1.37 | ..... | 2.29 | ..... | 2.61 | ..... |
| 17 | Kentucky ball clay | 13.90 | 34.70 | 8.43 | 37.50 | 3.46 | 39.02 | 2.45 | 40.55 | .98 | 41.25 |
| 18 | Tennessee ball clay | 9.00 | 36.90 | 3.77 | 39.12 | ..... | 40.50 | 2.29 | 41.80 | 1.71 | 42.75 |
| 19 | Tennessee | 4.05 | 39.01 | 1.38 | ..... | 1.07 | 40.80 | 1.32 | 39.50 | .72 | 40.20 |
| 20 | Southern Ohio | 9.75 | 20.95 | 7.39 | 22.32 | 3.58 | 23.75 | 1.19 | 24.20 | 5.66 | 20.90 |
| 21 | Southern Ohio, washed | 16.20 | 18.25 | 14.50 | 20.20 | 12.22 | 22.08 | 7.25 | 25.12 | .19 | 26.02 |
| | | | | | | 1225° C | | 1250° C | | 1285° C | |
| 22 | Maryland | 4.93 | 29.01 | 2.14 | 30.32 | 1.27 | 30.55 | .60 | 31.40 | 1.17 | 32.30 |
| 23 | Arkansas | 26.40 | 1.73 | 25.45 | 2.18 | 25.40 | 1.92 | 25.40 | 1.93 | 25.60 | 1.60 |
| 24 | Grossalmerode | 21.70 | 7.59 | 20.50 | 7.84 | 19.45 | 7.43 | 18.69 | 8.12 | 16.90 | 8.55 |
| 25 | Southern Illinois | 24.48 | 26.40 | 15.00 | 32.30 | 13.27 | 32.80 | 9.45 | 34.05 | 5.83 | 35.40 |
| 26 | Northern Illinois | 16.37 | 14.16 | 15.13 | 14.75 | 14.05 | 14.65 | 13.13 | 15.35 | 11.10 | 16.40 |
| 27 | St. Louis district | 16.35 | 18.76 | 15.45 | 19.60 | 13.72 | 21.10 | 11.61 | 22.30 | 8.96 | 23.25 |
| 28 | Mississippi | 15.76 | 23.30 | 14.10 | 23.10 | 12.92 | 23.30 | 9.87 | 24.20 | 5.95 | 25.65 |

**TABLE 2—Continued**

| No. | Source | 1320° C | | 1350° C | | 1400° C | | 1425° C | | 1450° C | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage | Porosity | Volume shrinkage |
| | | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| 1 | English ball clay | 2.20 | 34.35 | 2.31 | 31.32 | ..... | ..... | ..... | ..... | ..... | ..... |
| 2 | Klingenberg, A. T. | 1.49 | 32.32 | 1.56 | 29.75 | 1.59 | 30.70 | 1.48 | 26.64 | 3.93 | 16.35 |
| 3 | New Jersey | ..... | 10.83 | ..... | 7.78 | ..... | ..... | ..... | ..... | ..... | ..... |
| 4 | From a St. Louis firm | 2.09 | 19.34 | 13.75 | 12.78 | ..... | ..... | ..... | ..... | ..... | ..... |
| 5 | Klingenberg, E. T. | 2.19 | 38.00 | 2.47 | ..... | 2.42 | 36.40 | 3.23 | ..... | 3.53 | 26.85 |
| 6 | From a St. Louis firm | 1.85 | 38.65 | 2.08 | 38.30 | 2.09 | 39.55 | 1.85 | 38.22 | 4.61 | 34.05 |
| 7 | Kentucky | .97 | 42.75 | .81 | 42.60 | .95 | 42.80 | .33 | 42.10 | 3.30 | 37.62 |
| 8 | Southern Ohio | 2.50 | 18.18 | .52 | 13.78 | 4.56 | 14.21 | 6.01 | 9.08 | 5.60 | ..... |
| 9 | New Jersey | 2.97 | 40.10 | 1.16 | 40.35 | .71 | 40.25 | 1.33 | 37.90 | 5.45 | 31.25 |
| 10 | English ball clay | 1.38 | 27.87 | 1.59 | 28.65 | .82 | 28.50 | 2.34 | 24.90 | 3.03 | 19.95 |
| 11 | Southern Ohio | .09 | 20.65 | 2.83 | 16.20 | ..... | ..... | ..... | ..... | ..... | ..... |
| 12 | New Jersey | 11.88 | 32.15 | 8.60 | ..... | ..... | 33.45 | 6.68 | 35.00 | .84 | 36.35 |
| 13 | Tennessee ball clay | .17 | 35.10 | .38 | 34.10 | 1.28 | 33.10 | .48 | 28.50 | 4.89 | 20.20 |
| 14 | From a St. Louis firm | 10.82 | 8.14 | 16.90 | .75 | ..... | ..... | ..... | ..... | ..... | ..... |
| 15 | Southern Illinois | 2.07 | 39.40 | 2.27 | 39.10 | 2.53 | 40.00 | 2.15 | 38.90 | 2.72 | 35.15 |
| 16 | From a St. Louis firm | 5.62 | ..... | 6.01 | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 17 | Kentucky ball clay | 1.18 | 41.25 | 1.48 | 42.02 | .84 | 40.80 | 2.76 | 39.75 | 6.00 | 37.90 |
| 18 | Tennessee ball clay | 2.34 | 42.90 | 1.99 | 40.95 | 3.02 | 39.10 | 3.22 | 35.70 | 4.45 | 34.50 |
| 19 | Tennessee | 2.15 | 39.30 | 1.14 | 39.15 | .82 | 38.45 | 1.39 | 36.10 | 2.85 | 35.35 |
| 20 | Southern Ohio | 7.64 | 18.23 | 12.95 | 13.62 | ..... | ..... | ..... | ..... | ..... | ..... |
| 21 | Southern Ohio, washed | .71 | 27.60 | 1.46 | 26.32 | 3.56 | 25.41 | 7.02 | 17.95 | ..... | 12.92 |
| | | 1315° C | | | | 1390° C | | 1420° C | | | |
| 22 | Maryland | 1.47 | 32.35 | 1.53 | 30.70 | 2.44 | 28.85 | 5.92 | 22.25 | 7.95 | 18.60 |
| 23 | Arkansas | 24.95 | 1.82 | 25.05 | 1.81 | 25.02 | 1.94 | 24.40 | 2.12 | 23.90 | 2.24 |
| 24 | Grossalmerode | 15.53 | 9.67 | 14.10 | 9.68 | 12.25 | 10.70 | 11.85 | 10.60 | 6.95 | 8.64 |
| 25 | Southern Illinois | 5.09 | 38.12 | 3.30 | 38.40 | 2.86 | 38.60 | 3.13 | 38.40 | 3.92 | 37.38 |
| 26 | Northern Illinois | 9.44 | 17.25 | 7.98 | 17.38 | 5.75 | 19.23 | 4.32 | 19.65 | 3.08 | 18.85 |
| 27 | St. Louis district | 6.93 | 24.95 | 3.67 | 25.20 | 2.47 | 24.35 | 3.48 | 23.30 | 7.26 | 19.35 |
| 28 | Mississippi | 1.93 | 27.55 | 1.55 | 27.95 | 1.81 | 28.40 | 1.77 | 27.65 | 2.92 | 24.65 |

TABLE 2—Continued

| No. | Source | 1475° C | | 1500° C | | Softening temperature in cones | Remarks |
|---|---|---|---|---|---|---|---|
| | | Porosity | Volume shrinkage | Porosity | Volume shrinkage | | |
| | | Per cent | Per cent | Per cent | Per cent | | |
| 1 | English ball clay | ..... | ..... | ..... | ..... | 31½ | Overfired at 1320°. |
| 2 | Klingenberg, A. T. | 6.02 | ..... | 3.79 | ..... | 32 | Overfired at 1450°. Sensitive to sudden cooling. |
| 3 | New Jersey | ..... | ..... | ..... | ..... | 27½ | Begins to overfire at 1230°. |
| 4 | From a St. Louis firm | ..... | ..... | ..... | ..... | 27 | Overfired decidedly at 1350°. |
| 5 | Klingenberg, E. T. | ..... | ..... | 3.79 | ..... | 32 | Cracked in drying and burning. Overfired at 1450°. |
| 6 | From a St. Louis firm | 6.54 | 25.32 | 7.01 | ..... | 32 | Overfired at 1450°. |
| 7 | Kentucky | 4.88 | 32.90 | 7.13 | ..... | 32½ | Do. |
| 8 | Southern Ohio | ..... | ..... | ..... | ..... | 31 | Begins to overfire at 1400°. |
| 9 | New Jersey | 3.85 | 25.30 | 5.30 | 23.80 | 32 | Overfired at 1450°. |
| 10 | English ball clay | 3.05 | ..... | 6.95 | ..... | 32 | Overfired at 1425°. |
| 11 | Southern Ohio | ..... | ..... | ..... | ..... | 30½ | Overfired at 1350°. |
| 12 | New Jersey | .15 | 34.00 | 1.77 | 29.78 | 32 | Overfired at 1500°. |
| 13 | Tennessee ball clay | 2.90 | 16.28 | 6.03 | ..... | 32 | Overfired at 1425°. |
| 14 | From a St. Louis firm | ..... | ..... | ..... | ..... | 27 | Overfired at 1320°. |
| 15 | Southern Illinois | 4.38 | 28.35 | 5.82 | 26.85 | 32 | Overfired at 1450°. |
| 16 | From a St. Louis firm | ..... | ..... | ..... | ..... | ..... | Overfired at 1320°. |
| 17 | Kentucky ball clay | ..... | ..... | 4.85 | 35.60 | 32 | Overfired at 1450.° |
| 18 | Tennessee ball clay | ..... | ..... | 5.80 | 33.40 | +32 | Overfired at 1425°. |
| 19 | Tennessee | ..... | ..... | 5.18 | ..... | +32 | Overfired at 1450°. |
| 20 | Southern Ohio | ..... | ..... | ..... | ..... | 30½ | Overfired at 1290°. |
| 21 | Southern Ohio, washed | ..... | ..... | ..... | ..... | 21½ | Overfired at 1400°. |
| | | 1480° C | | | | | |
| 22 | Maryland | 6.95 | 19.00 | 4.90 | 18.65 | 31 | Begins to overfire at 1390°. |
| 23 | Arkansas | 22.55 | 2.69 | ..... | ..... | 29 | Does not overfire at 1475°+. |
| | | | | 1505° C | | | |
| 24 | Grossalmerode | 11.90 | 4.73 | 26.20 | 11.1 | 29 | Overfired at 1480°. |
| 25 | Southern Illinois | 4.54 | 34.50 | 10.25 | 30.80 | +32 | Overfired at 1475°. |
| | | 1470° C | | | | | |
| 26 | Northern Illinois | 1.92 | 18.90 | ..... | ..... | 29 | Not yet overfired at 1475°. |
| 27 | St. Louis district | 10.50 | 18.10 | ..... | ..... | 31 | Overfired at 1450°. |
| 28 | Mississippi | 8.63 | 19.95 | ..... | ..... | 30 | Begins to overfire at 1450°. |

## IV. DISCUSSION OF THE INDIVIDUAL CLAYS

*No. 1, English Ball Clay.*—This clay possesses sufficient strength to be classed as a bond clay, its modulus being 376 pounds per square inch. It vitrifies at 1150° C and overfires distinctly at

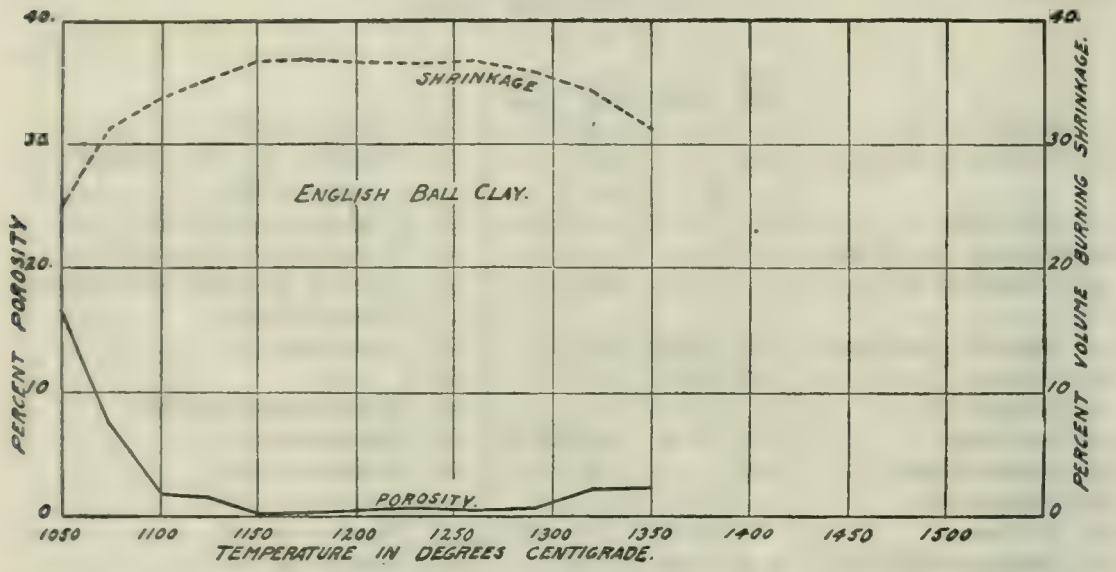


FIG. 1.—*Diagram showing contraction with temperature of English ball clay (No. 1)*

1320° C, but not seriously. Its porosity and volume changes with temperature are shown in Fig. 1. From the contraction curve it appears, as shown by the downward trend of the curve, that swelling begins at about 1300° C. The material, therefore, is not prom-

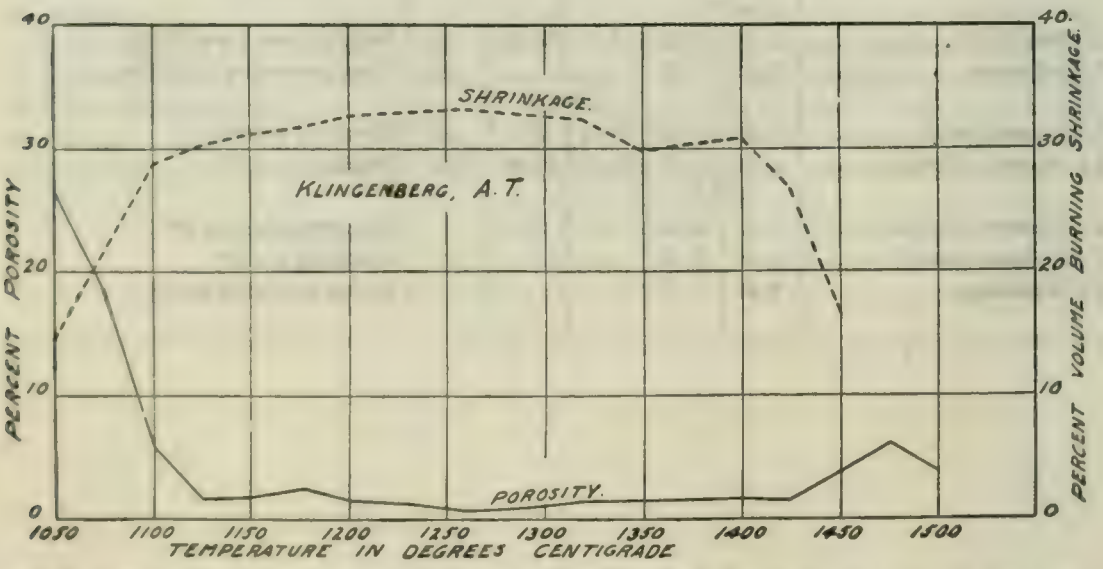


FIG. 2.—*Diagram showing contraction with temperature of Klingenberg clay, A. T. brand*

ising for steel-melting crucibles and for glass refractories, though it might be satisfactory for brass-melting crucibles.

*No. 2, Klingenberg, A. T.*—The bonding power of this clay is not of an extraordinary quality and, in fact, is inferior to that of

some American clays. In addition, its tendency to crack badly in drying is an undesirable feature. It has, of course, ample mechanical strength for the purpose for which it is used, the making of graphite crucibles. From Fig. 2 it will be seen that it vitrifies at 1125° C and remains remarkably constant in structure up to 1425° C. At this point overfiring begins, as is shown particularly by the volume curve, which indicates decided bloating, so that at 1450° C the clay has about the same volume it had at 1050° C before vitrification took place. At 1450° C it is, therefore, decidedly overfired. However, its excellent burning behavior is apparent from the long temperature range. It would not be a satisfactory glass refractory. One disadvantage of this material is its extreme sensitiveness to sudden heating and cooling as it shatters very readily under such conditions. Its softening temperature is satisfactory.

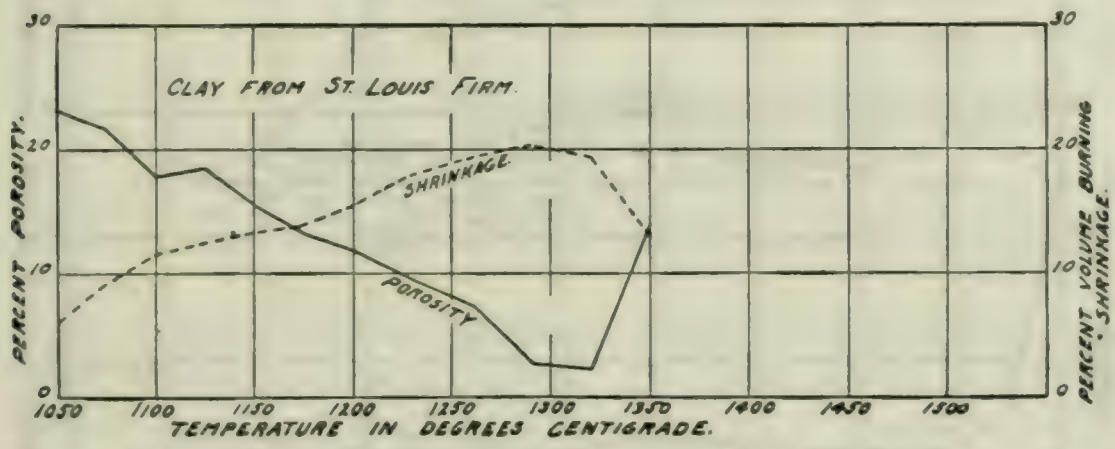


FIG. 3.—*Diagram showing contraction with temperature of clay from St. Louis firm (No. 4)*

*No. 3, New Jersey Clay.*—This clay is of a siliceous nature, and, while it possesses excellent strength in the unmixed state, it is somewhat deficient in bonding power, as indicated by its low modulus when admixed with sand, 255 pounds per square inch. In burning it reaches the vitrified state at 1200° C. and shows evidence of overfiring by decided swelling at 1230° C. These results, together with its low softening point, should exclude it from use as a high-grade bond clay.

*No. 4, Clay from a St. Louis Firm.*—This material is an excellent one from the standpoint of plasticity, bonding power, and strength. It shows a modulus of 399 pounds per square inch. It becomes dense at 1290° C, but overfires at 1320° C, and at 1350° C it has developed a decided vesicular structure, indicated both by the volume and porosity changes, as shown in Fig. 3. Its softening point is that of cone 27. The material must, therefore, be rejected as a high-grade bond clay.

*No. 5, Klingenberg, E. T.*—This clay is of a sticky nature and possesses good plasticity and bonding power, its modulus being 363 pounds per square inch. It has a strong tendency to check and crack in drying. In burning it becomes dense at 1100° C, and it shows an extraordinary temperature range up to 1400° C. It begins to bloat at this temperature although its porosity is not decidedly increased, even at 1450° C. As is seen in Fig. 4, the volume change is especially useful in indicating the structural changes taking place. It is interesting also to observe the high resistance of the dried clay to the disintegrating action of water.

*No. 6, Clay from a St. Louis Firm.*—The clay is a satisfactory one from the standpoint of its physical properties in the raw state. It shows a modulus of rupture of 351 pounds per square inch. It becomes quite dense at 1200° C and starts to overfire at about

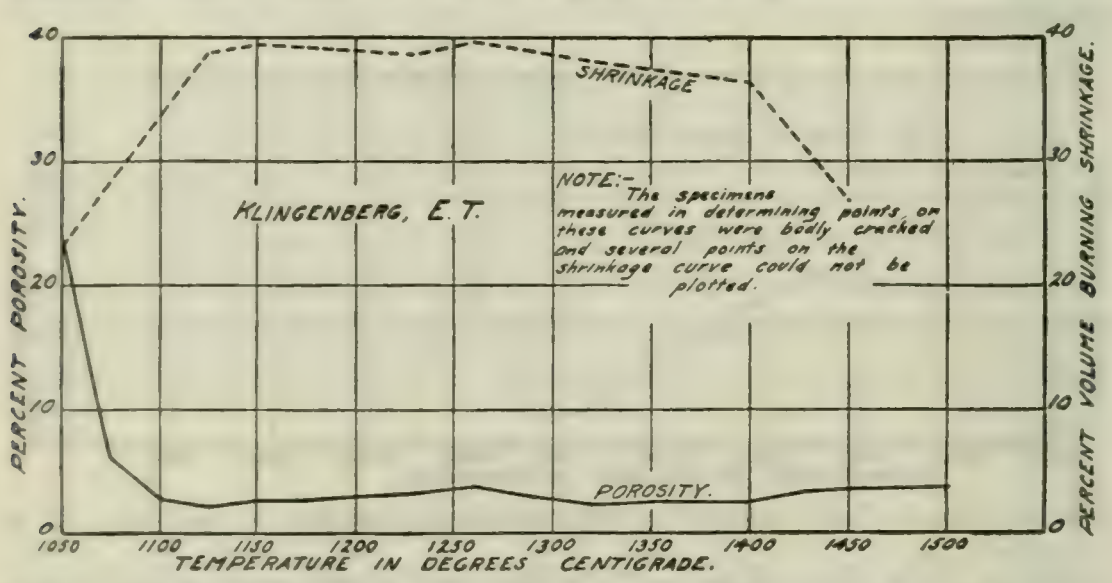


FIG. 4.—*Diagram showing contraction with temperature of Klingenberg clay, E. T. brand*

1430° C, this condition being distinctly shown at 1450° C. It shows, thus, an excellent temperature range. Its propensity to bloat at this temperature is quite evident. Its refractoriness is satisfactory, the softening point being equivalent to that of cone 32. The clay seems very promising as a crucible material.

*No. 7, Kentucky.*—This material is very plastic, but is lacking in bonding power, as indicated by the low modulus, 234 pounds per square inch. This might be inferred also from the high ratio of pore to shrinkage water, which is 1.05. The specific gravity, 1.55, is below the average of such clays. The clay vitrifies to a dense structure at about 1260° C and remains quite constant up to 1425° C, where it begins to overfire. At 1450° C it shows distinct evidence of this change. (See Fig. 5.) Its refractoriness, corresponding to that of cone 32, is satisfactory. This clay could be

used in conjunction with a stronger clay as a bonding material for crucibles, but would hardly be suitable for this purpose if used alone. It might be used also for glass refractories with other clays of somewhat different properties. The high porosity of the clay at 1050° C, 37 per cent, is indicative of its open structure in the

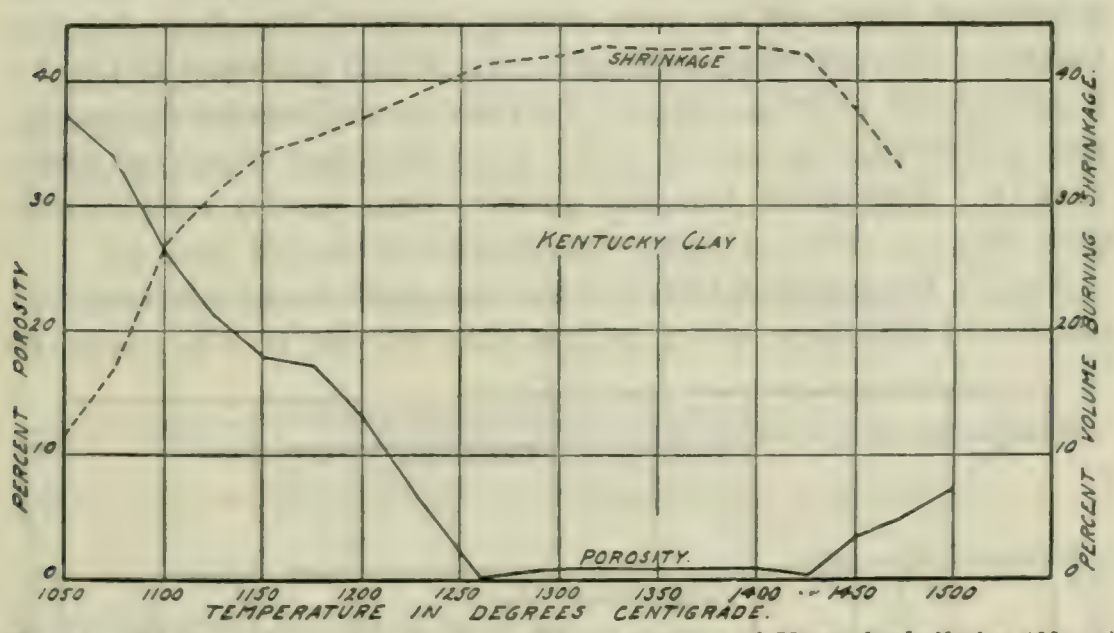


FIG. 5.—*Diagram showing contraction with temperature of Kentucky ball clay (No. 7)*

dried state and explains the ready disintegration of the raw clay in water.

*No. 8, Southern Ohio.*—This clay, though quite plastic, is somewhat deficient in bonding power. Its modulus with sand is 281 pounds, but its strength without admixture is considerable, 479

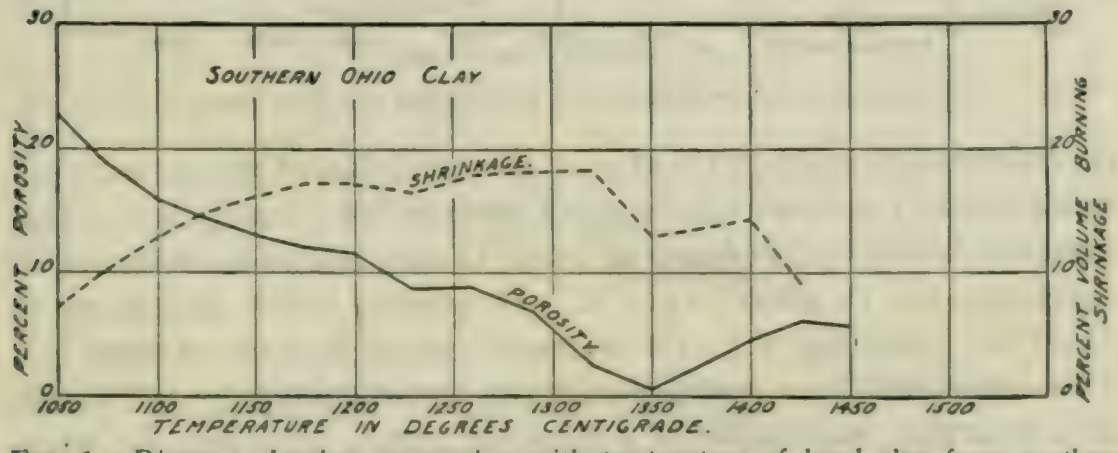


FIG. 6.—*Diagram showing contraction with temperature of bond clay from southern Ohio (No. 8)*

pounds. Its specific gravity in the dried state is above the average and indicates a dense structure, which is verified by its low porosity, 22.83 per cent at 1050° C. The clay burns to dense vitrification at 1350° C and begins to overfire soon after this temperature has been reached. At 1400° C it is distinctly vesicular. (See Fig. 6.)

It softens at cone 31. The material is not of the highest type, though it could be used in a mixture with other clays.

*No. 9, New Jersey.*—The low strength of this clay in the dry state would prohibit its use as a bond clay by itself. It has, however, good burning qualities, which would render it suitable for admixture with one or more strong clays of the dense-burning variety. The clay is of a siliceous nature and possesses at 1050° C a porosity of 40.80 per cent. Its rate of vitrification is gradual, and it becomes dense at 1350° C. Overfiring starts at about 1425° C. Expansion becomes quite evident at this temperature. (See Fig. 7.) The softening temperature is that of cone 32.

*No. 10, English Ball Clay.*—This clay, with its satisfactory proportion of shrinkage water to true clay volume 60.8 per cent, its

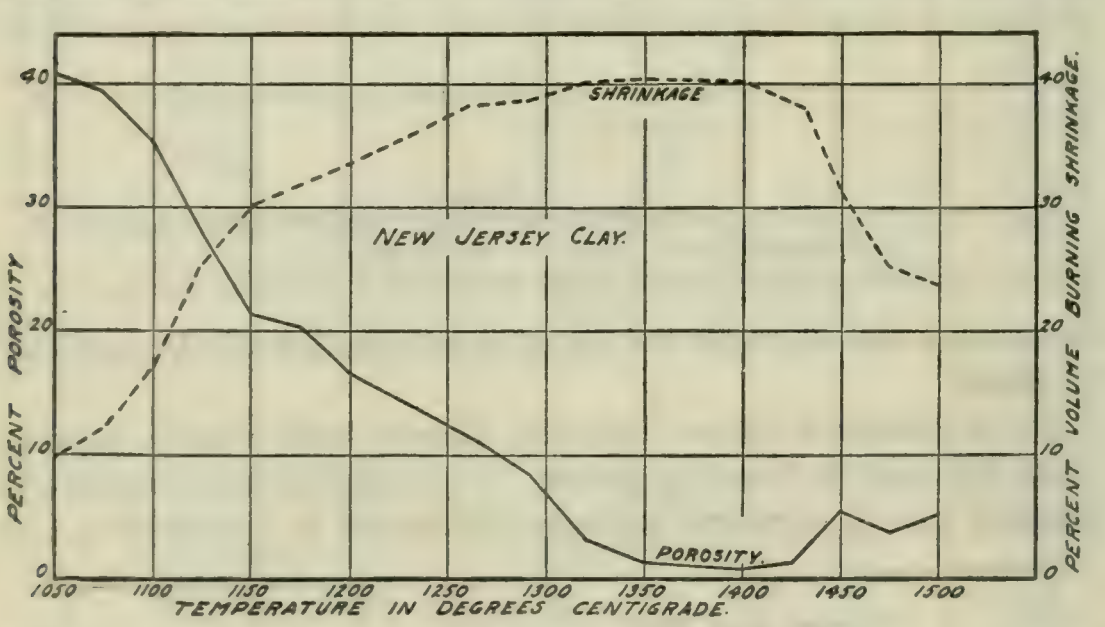


FIG. 7.—*Diagram showing contraction with temperature of a New Jersey clay (No. 9)*

pore-shrinkage water ratio of 0.75 and modulus of 389 pounds per square inch, possesses all the good qualities of a bond clay. This material burns quite dense at 1125° C and shows no evidence of overfiring up to about 1415° C. Overfiring is not serious up to 1450° C. (See Fig. 8.) Its softening point is that of cone 32. This clay should be a useful one for the crucible industry and would be a desirable constituent of a glass-pot batch, especially for melting corrosive glasses where a dense pot structure is required.

*No. 11, Southern Ohio.*—This clay is somewhat similar to sample No. 8.

*No. 12, New Jersey.*—This clay is of a siliceous character and is lacking in bonding power to such an extent that it would be

ruled out from the bond-clay class. Its firing behavior is that of a siliceous clay, low in fluxes. It becomes very dense at 1475° C

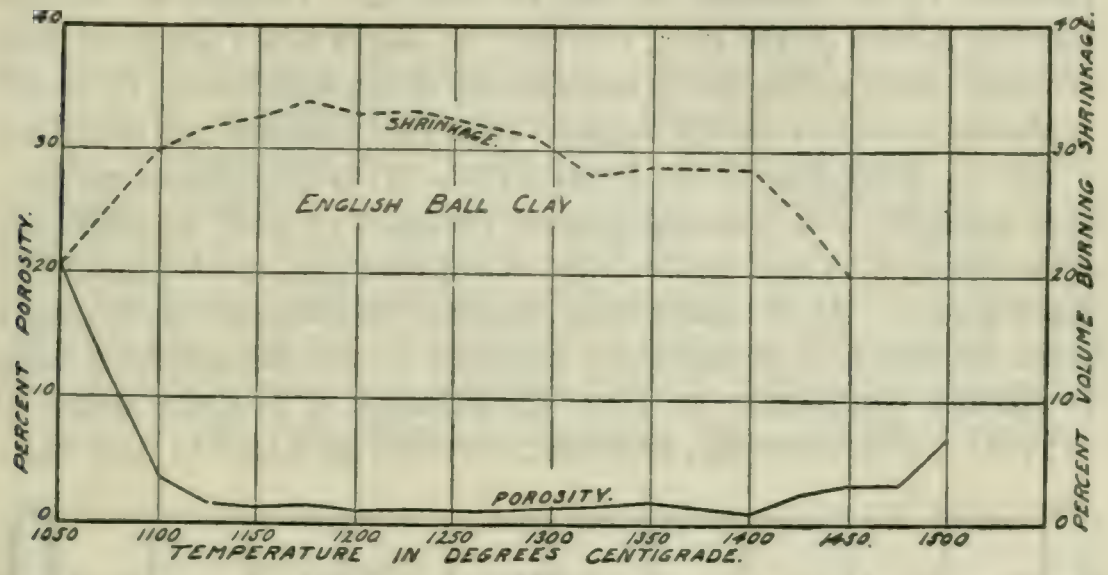


FIG. 8.—*Diagram showing contraction with temperature of an English ball clay (No. 10)*

and begins to overfire beyond this point. (See Fig. 9.) Its softening point is that of cone 32.

*No. 13, Tennessee.*—This clay, although of excellent plasticity, is lacking in bonding power, as indicated by its modulus of 200

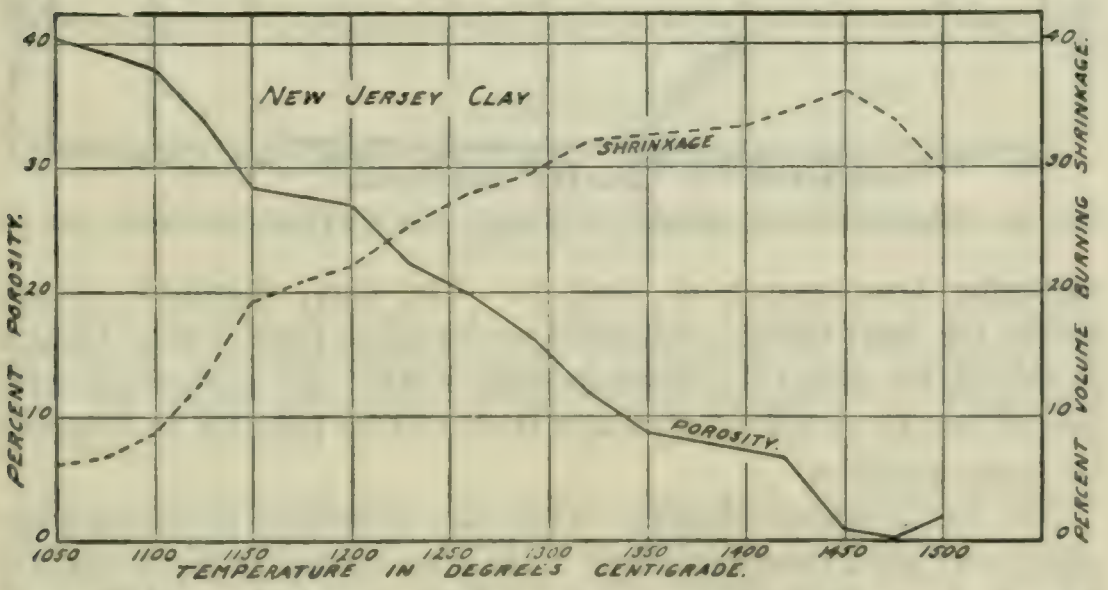


FIG. 9.—*Diagram showing contraction with temperature of a New Jersey plastic clay (No. 12)*

pounds. At 1050° C it has a porosity of 33.5 per cent and vitrifies gradually, reaching maximum density of structure at about 1260° C. Practically constant porosity is maintained up to about 1425° C

when overfiring begins. (See Fig. 10.) At this point expansion of the clay volume is quite evident. The softening temperature of the material is that of cone 32. In spite of the low bonding power of the clay, it would be useful when admixed with stronger clays, owing to its satisfactory firing behavior. It would probably be better suited for steel than for brass melting crucibles.

*No. 14, Clay from a St. Louis Firm.*—This clay shows remarkable strength and bonding power, its ratio of pore to shrinkage water being 0.54 and its modulus of rupture 554, the highest of all clays tested. At the same time, it offers no difficulty in drying, a point in which it is decidedly superior to the Klingenberg clay. It vitrifies completely at 1200° C, although it is quite dense at 1175° C. The material, however, overfires at 1320° C and has a

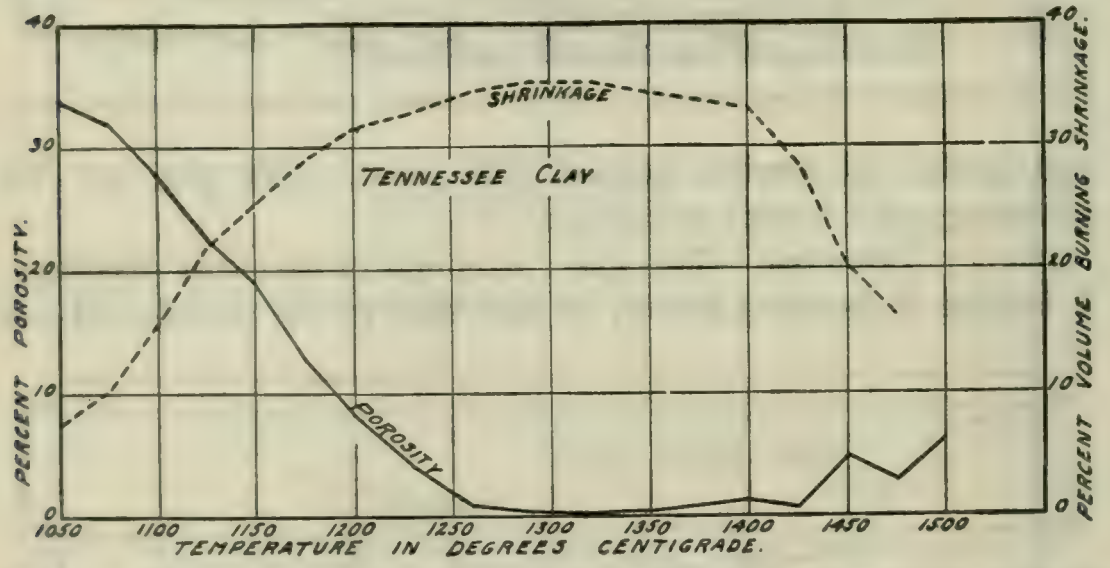


FIG. 10.—*Diagram showing contraction with temperature of a Tennessee ball clay (No. 13)*

softening temperature of cone 27. The clay, therefore, is not suited for steel-melting crucibles or for glass refractories, though it should be useful for brass-melting work. By admixture with one or two more refractory clays it should be possible to improve its firing qualities.

*No. 15, Southern Illinois.*—This clay possesses excellent plasticity and good bonding power. Its pore-shrinkage water ratio is 0.65 and its modulus 341 pounds. The porosity at 1050° C is 34.5 per cent, and the clay becomes dense, though not completely vitrified, at about 1230° C. Overfiring does not begin until a temperature of 1450° C has been reached. The temperature range of this clay is, therefore, a very long one. Overfiring does not take place quickly, but evidently is a gradual process. (See Fig. 11.) The softening point is that of cone 32. The clay is un-

questionably one of the best bond clays examined, especially for glass refractories.

*No. 16, Clay from a St. Louis Firm.*—This clay possesses good plasticity and bonding power, since its modulus is 351 pounds. In burning, however, it overfires at 1320° C and for this reason can not be considered of particular promise.

*No. 17, Kentucky Ball Clay.*—This clay possesses excellent working qualities and good strength. Its shrinkage water content is very high, being 77.4 per cent, in terms of the true-clay volume; its porosity-shrinkage water ratio is 0.71 and its modulus 362. Its porosity at 1050° C is 37.8 per cent, and it burns to complete vitrification at about 1290° C. It begins to overfire at 1400° C, but this change is a gradual one. Its softening tem-

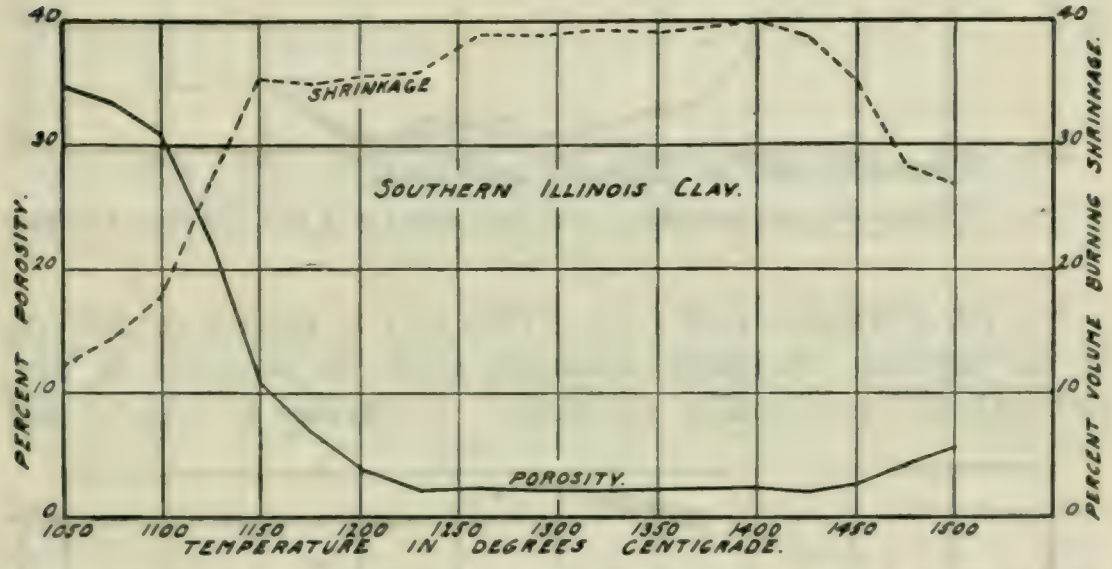


FIG. 11.—*Diagram showing contraction with temperature of a bond clay from southern Illinois (No. 15)*

perature is that of cone 32. The clay, therefore, is an excellent bond clay, especially suitable for steel-melting crucibles and also for glass refractories. Its firing behavior is illustrated graphically in Fig. 12.

*No. 18, Tennessee Ball Clay.*—Although this material possesses excellent plasticity, it is somewhat deficient in bonding power, as indicated by its high pore-shrinkage water ratio, 0.95, and its low modulus, 228 pounds. On the other hand, its firing behavior is excellent. It vitrifies at about 1230° C from a porosity of 37.50 per cent at 1050° C. It remains very constant in structure till 1400° C is reached, when it begins to overfire very gradually. It still possesses a good structure at 1450° C. The softening point corresponds to that of cone 32+. It is undoubtedly a valuable

clay, chiefly on account of its good firing qualities. It is especially suitable for glass refractories, but for crucible work it requires admixture with a somewhat stronger clay. The firing qualities of this material are illustrated in Fig. 13.

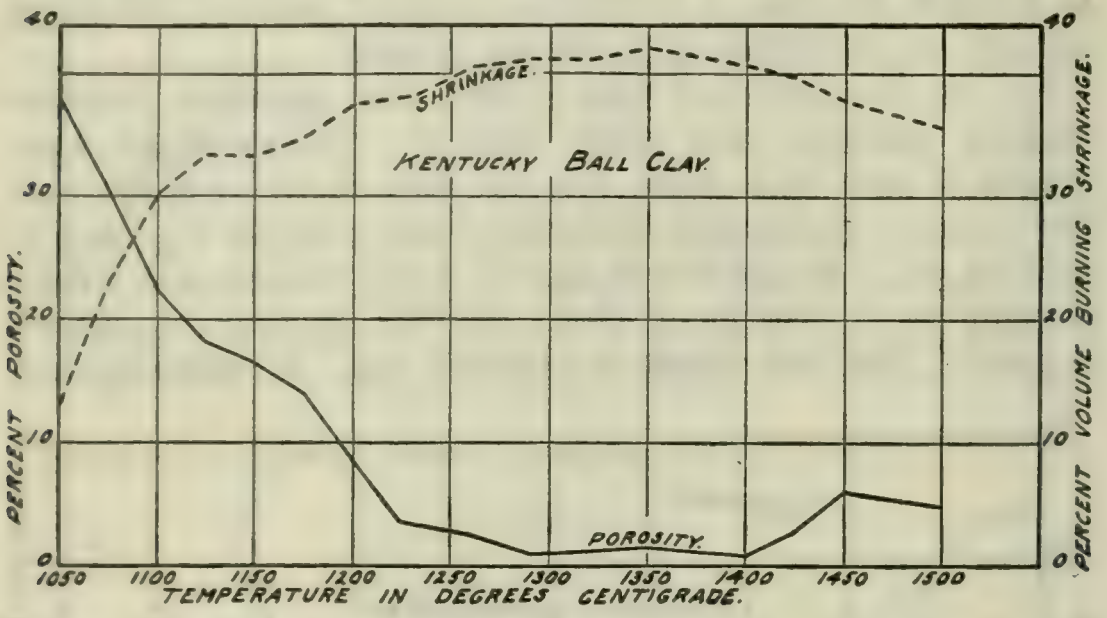


FIG. 12.—*Diagram showing contraction with temperature of a ball clay from Kentucky (No. 17)*

*No. 19, Tennessee Ball Clay.*—This clay is similar to No. 18, It is, however, decidedly stronger, since its modulus is 282, although it has a smaller shrinkage. It vitrifies at 1200° C and

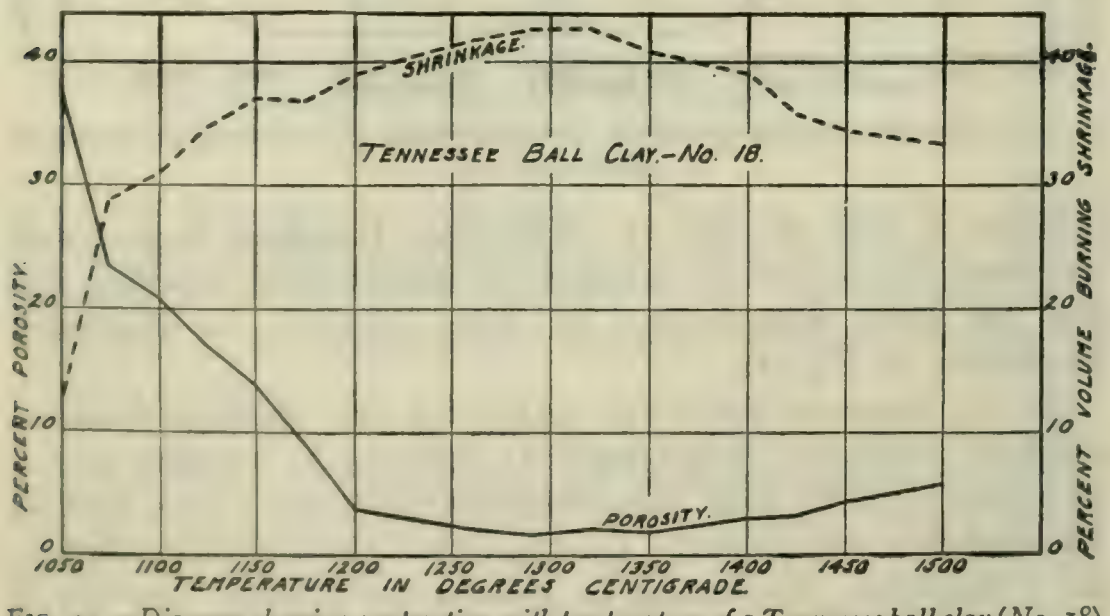


FIG. 13.—*Diagram showing contraction with temperature of a Tennessee ball clay (No. 18)*

does not begin to overfire before 1425° C. At 1450° C it still shows a good structure. The overfiring takes place gradually, as is seen from Fig. 14. Its softening temperature is about cone 32.

What has been said of the previous clay applies also to this material, though it might be said to be superior to No. 18.

*No. 20, Southern Ohio.*—This clay is very plastic and possesses satisfactory bonding power. Its pore-shrinkage water ratio is 0.72 and its modulus 321. Its water content is considerably

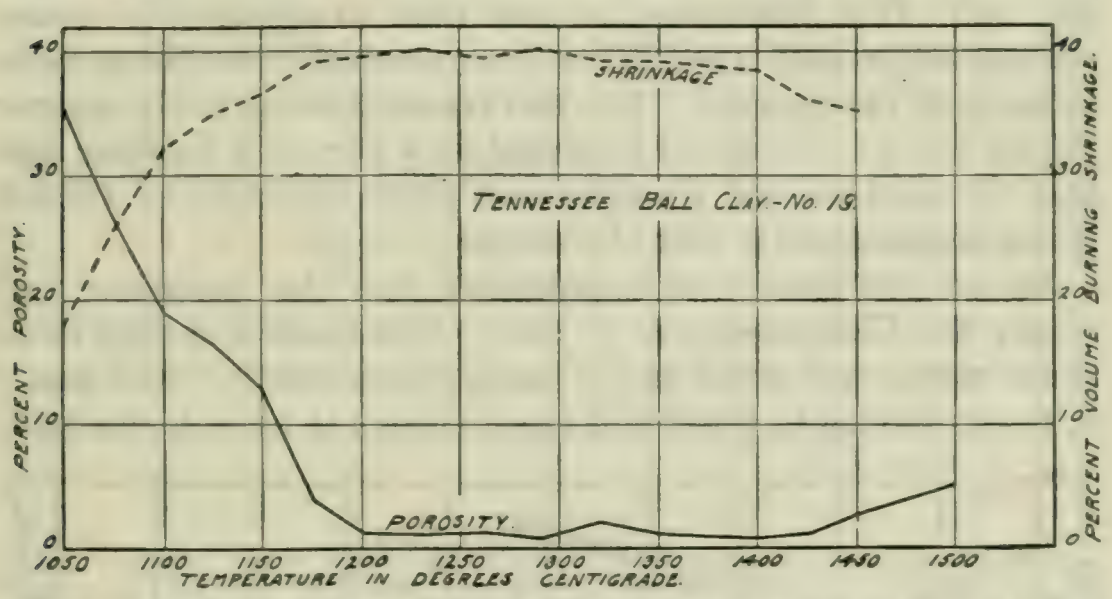


FIG. 14.—*Diagram showing contraction with temperature of a Tennessee ball clay (No. 19)*

below the average values holding for the other clays, since it is only 39.7 per cent of the true-clay volume. For this reason the density of the molded clay is quite high, the specific gravity being 1.91. The porosity at 1050° C is only 22.30 per cent, and

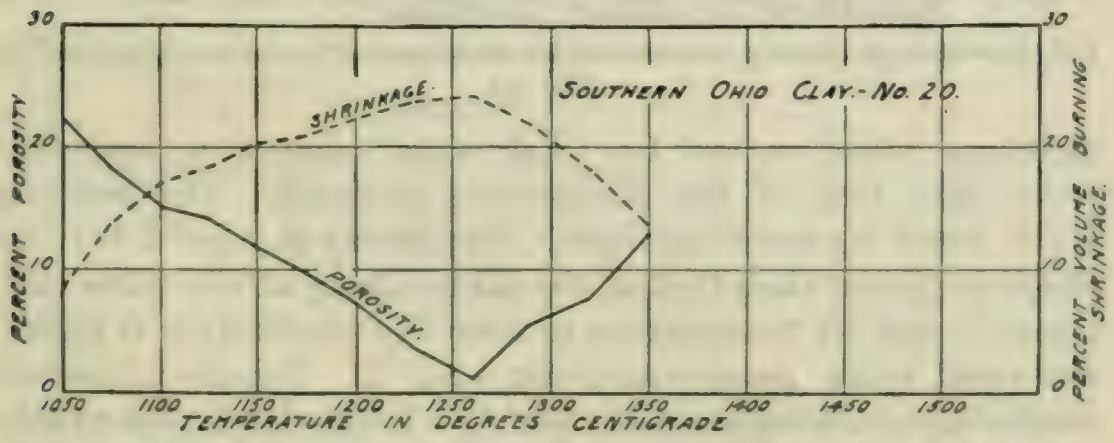


FIG. 15.—*Diagram showing contraction with temperature of a southern Ohio bond clay (No. 20)*

it vitrifies completely at 1260° C, beginning to overfire immediately. (See Fig. 15.) The softening point is that of cone 30½. It cannot be considered a bond clay of the highest type in view of these results, and, in any event, it should not be used alone, but invariably in conjunction with other clays.

*No. 21, Southern Ohio.*—This clay is similar to No. 20. It is not quite so strong as the former, indicated both by the higher pore-shrinkage water ratio, 0.87, and by the lower modulus, 277. It vitrifies more gradually, becoming completely dense at 1290° C and overfiring slowly beyond this temperature. (See Fig. 16.) It is interesting to note that no appreciable volume changes occur until 1400° C has been reached, a condition much in favor of the material. For this reason it is distinctly superior to clay No. 20. It should be useful as a part of a bonding mixture for steel-melting crucibles and glass refractories. Its softening temperature is that of cone 31½.

*No. 22, Maryland.*—In appearances this clay resembles very closely the Klingenberg, A. T. clay. It is black and high in organic matter and exhibits the same characteristic "stickiness." It resists slaking in water still more, though it has a higher pore-

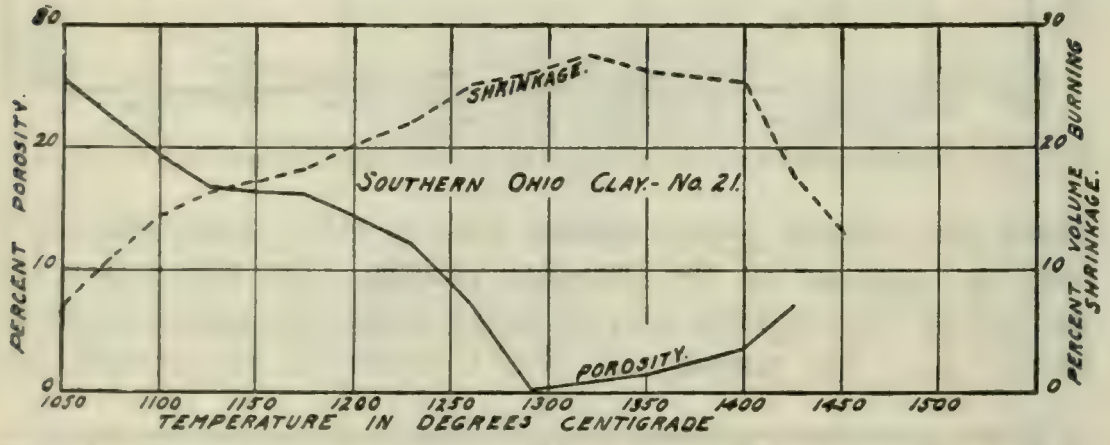


FIG. 16.—*Diagram showing contraction with temperature of a southern Ohio bond clay (No. 21)*

shrinkage water ratio. Its total water content is somewhat lower than that of the Klingenberg material. The modulus is 518, which is exceedingly high. Its porosity at 1090° C is 21.80, which is greater than that of the Klingenberg at the same temperature, and its temperature of complete vitrification is higher, this point being reached at about 1250° C. The clay, however, reaches a good dense state at 1200° C. Expansion begins to take place somewhat below 1350° C, and this change becomes accelerated markedly at 1400° C, followed by a stage of quiescence. This material evidently becomes quite viscous at temperatures above 1450° C. (See Fig. 17.) The softening point is that of cone 31. It would seem that this clay should be valuable for the crucible industry, though less suitable for glass refractories.

*No. 23, Arkansas.*—This clay is of the type of the Grossalmerode clay. It is siliceous in character and evidently very

low in fluxing materials. It possesses excellent plasticity and bonding power, being superior in this respect to the German clay. Its required water content is higher than that of the imported material, amounting to 75.3 per cent, in terms of the true-clay volume. Its pore-shrinkage water ratio also more

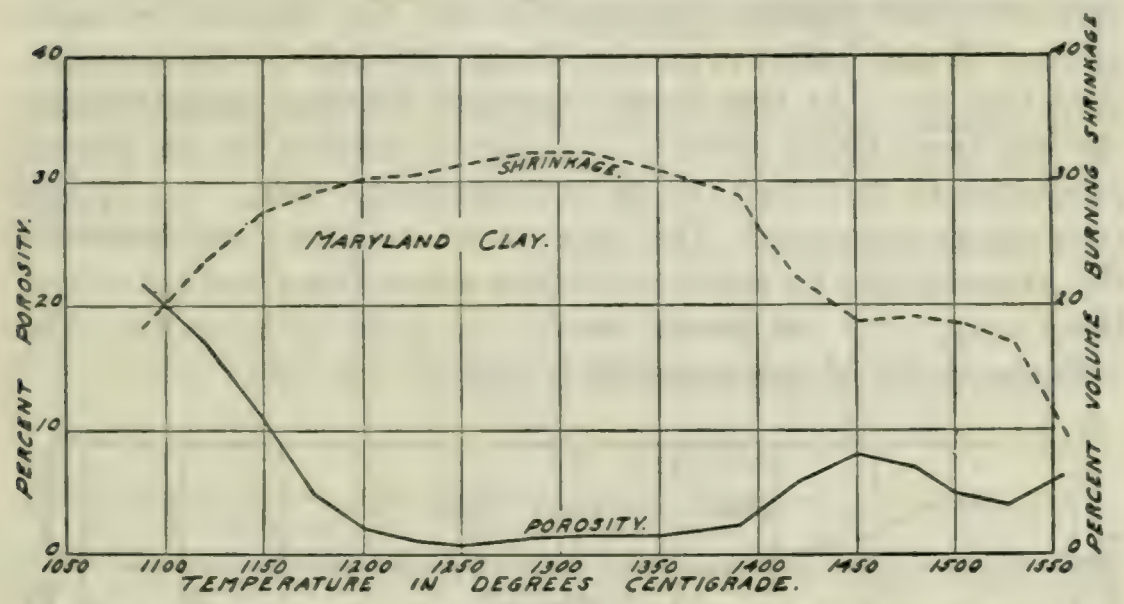


FIG. 17.—*Diagram showing contraction with temperature of a Maryland bond clay (No. 22)*

favorable, being 0.72. The modulus is 466 pounds. The burning behavior, likewise, is superior to that of the German clay, as may be seen from Fig. 18. It does not vitrify at all within the temperature range employed, its porosity at 1450° C being

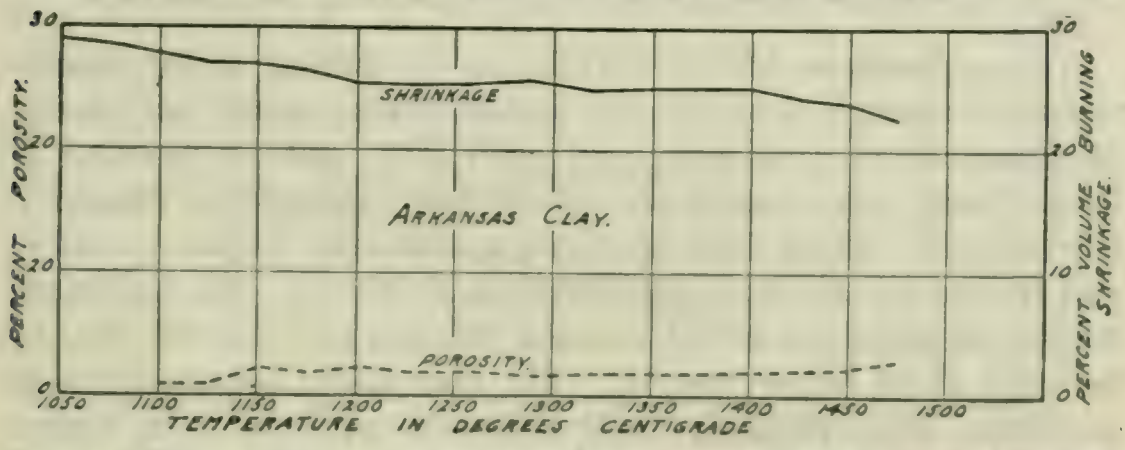


FIG. 18.—*Diagram showing contraction with temperature of an Arkansas bond clay (No. 23)*

still 23.90 per cent. The volume remains remarkably constant. The softening point is that of cone 29. It is evident that this clay is an excellent glass-pot material. though not adapted to crucible work, except in connection with another stronger but more dense burning refractory material.

*No. 24, Grossalmerode.*—This well-known clay is very plastic, though its pore-shrinkage water ratio is high, 0.99, characteristic of siliceous clays. Its specific gravity in the dried state is high, it being 1.99. Its bonding power is indicated by the modulus, 364 pounds per square inch. It burns to a strong, but still somewhat porous, structure, showing 6.95 per cent porosity, at 1450° C, and begins to overfire shortly beyond this temperature. (See Fig. 19.) At this point expansion becomes quite evident. As has been stated before, this clay is inferior in its general properties to clay No. 23, its only advantage being that it fires to a denser structure. The same result could be obtained with the Arkansas clay by admixture with a denser firing, but refractory, bond clay, and the result would be more satisfactory. The softening point of this material is that of cone 29.

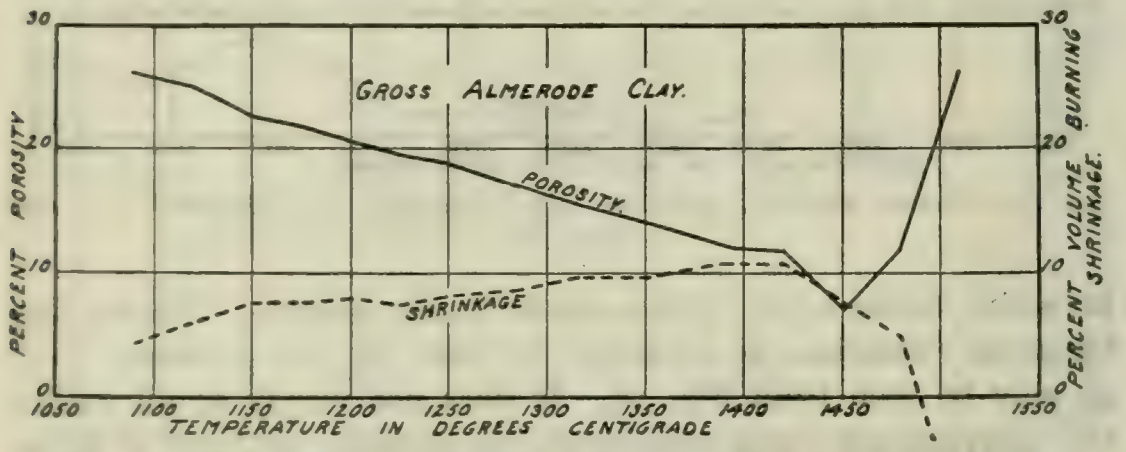


FIG. 19.—*Diagram showing contraction with temperature of Grossalmerode clay.*

*No. 25, Southern Illinois.*—This clay is similiar in its characteristics to sample No. 15. Its pore-shrinkage water ratio is not so favorable, 0.75, as compared with 0.65, and its modulus is lower, being 262 pounds per square inch, though its plasticity is excellent. When fired, it shows a somewhat higher porosity, and it does not become quite as dense as No. 15. Its maximum density of structure is not reached before 1350° C, while No. 15 becomes dense below 1250° C. The clay under consideration is somewhat more refractory and begins to over-fire at a higher temperature. (See Fig. 20.) Its softening point is that of cone 32+. In spite of its lower bonding power, this clay should be very useful as a general refractory bond clay, especially for steel-melting crucibles and glass pots. It should be used in connection with somewhat stronger bond clays.

*No. 26, Northern Illinois.*—This No. 2 fire clay shows the lowest water content of any of these clays. The per cent of shrinkage

water in terms of the true-clay volume is only 27.3 and the pore-shrinkage water ratio is 0.89. The material shows fair plasticity and its modulus is 240. The siliceous character of the clay is indicated by the porosity-temperature diagram (See Fig. 21.)

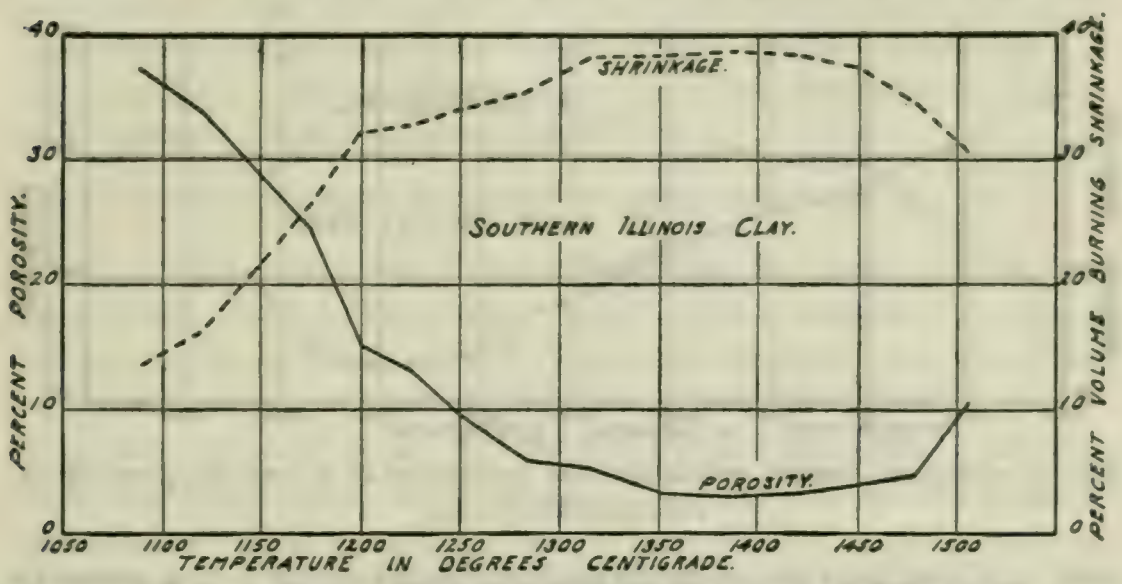


FIG. 20.—*Diagram showing contraction with temperature of southern Illinois bond clay (No. 25)*

It is of the Grossalmerode type and shows a steady progress of vitrification. Over-firing was not yet observed at 1475° C. From the burning standpoint the material is a very excellent one. The softening point corresponds to that of cone 29. It is evident that this clay is a useful one, especially when blended with such

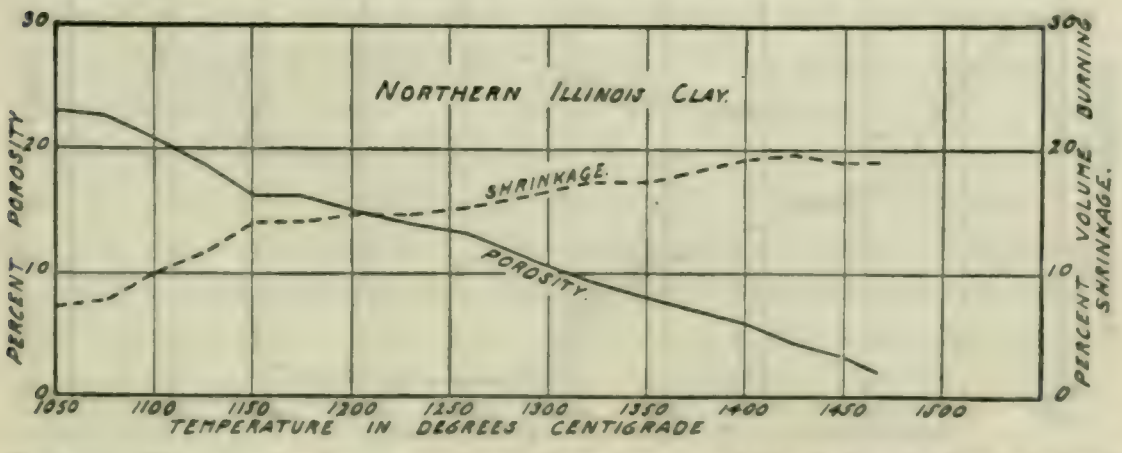


FIG. 21.—*Diagram showing contraction with temperature of plastic fire clay from northern Illinois (No. 26)*

a material as No. 15. Its primary use would be in connection with glass refractories, although, together with a clay like No. 22, it would produce a good crucible mixture, adjusted to produce the desired density of structure at a lower temperature.

*No. 27, St. Louis District.*—This is a typical clay from this district, of good plasticity, but somewhat deficient in bonding power. The pore-shrinkage water ratio is 0.74 and the modulus is 263 pounds per square inch. Its porosity at 1050° C is 25 per

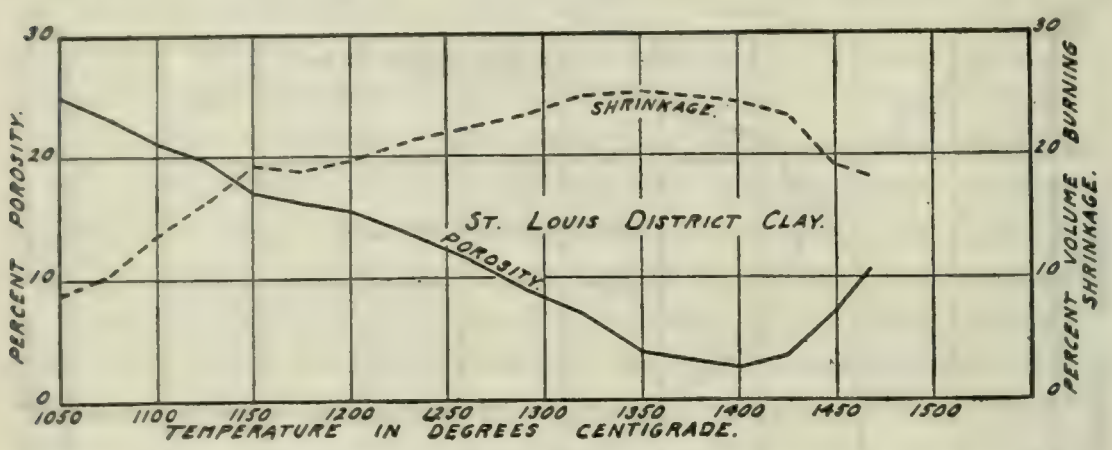


FIG. 22.—*Diagram showing contraction with temperature of a bond clay from the St. Louis district (No. 27)*

cent, and vitrification proceeds uniformly and steadily to a porosity of 2.5 per cent at 1400° C. It does not begin to overfire till 1425° C is reached. (See Fig. 22.) It is, therefore, a very satisfactorily burning material. Here, again, it should be stated that the best results are obtained in admixture of this clay with a clay of

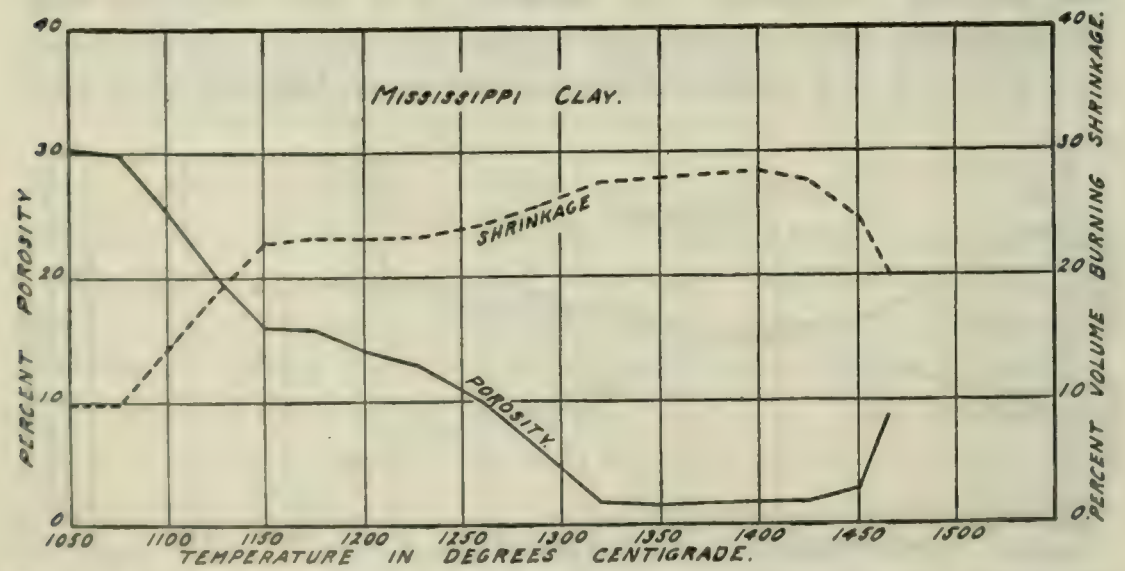


FIG. 23.—*Diagram showing contraction with temperature of a bond clay from Mississippi (No. 28)*

greater bonding power and supplementing its burning characteristics. The softening point is that of cone 31.

*No. 28, Mississippi.*—This bond clay is of a slightly "sticky" nature, somewhat inclined to crack in drying. Its pore-shrinkage

water ratio is 0.81, and its bonding power is very acceptable, as indicated by its modulus, which is 326 pounds per square inch. Beginning with a porosity of 30 per cent at 1050° C, it vitrifies quite gradually, becoming dense at 1320° C. This condition is maintained constant up to 1450° C, where overfiring occurs, indicated by expansion on the volume change curve. (See Fig. 23.) The softening point is that of cone 30. The clay should be generally useful as a bonding material.

### V. CONCLUSIONS REGARDING AMERICAN BOND CLAYS

The results here given furnish proof for the assertion that we have in the United States clays which make possible the manufacture of the several kinds of refractories without the use of imported materials. The fact should be emphasized that in nearly every case the use of an intimately blended mixture of suitable clays is to be preferred to the use of single clays. In this manner, using such data as have been here presented, it should be possible to produce bodies possessing all the desired properties. Very similar clays should not be worked together. To illustrate this statement, we might say, for instance, that clay No. 23 (Arkansas) should be blended with clay No. 27 (St. Louis district) for glass refractories. In this manner, by the use of clays which show certain contrasts, it would be possible to exercise accurate control over the resulting qualities, and hence to secure the best commercial results. A clay like No. 22 (Maryland) should be supplemented by such clays as Nos. 7 (Kentucky), No. 13 (Tennessee), or Nos. 18 and 19 (Tennessee). Again, No. 14 would be improved by mixture with Nos. 15, 25, or 26 (Illinois). It is evident that in this fashion more or less dense, or, again, open, burning bodies may be produced according to the specific needs of each case. It is very much to be urged that systematic methods of studying these raw materials replace the cut-and-try procedures which are only too common. For glass refractories a siliceous clay should be used as the basis, and this should be reinforced by the addition of suitable dense-burning materials.

It goes without saying that there are many clays of the bond-clay type in the United States. In addition, there are available the plastic kaolins, which, though they would not contribute toward the strength of the body, are very effective in increasing the refractoriness and raising the overfiring temperature. In this laboratory the use of Georgia and Florida kaolins, in percentages up to 20 of the total clay employed, has been found to be very

effective for high-grade bodies. At the prevailing prices of No. 1 bond clays the use of the unwashed Georgia kaolins would not be prohibitive.

Some mistakes have been made in the hurry to develop promising clay properties. These errors consist in including in shipments entirely unsuitable clays adjoining the strata of good clay, poor judgment in differentiating the different clays, the failure to reject obvious impurities, such as pyrites or gypsum, and especially in failing to make a comprehensive and thorough survey of the deposits, both by borings and by the sinking of shafts. As a result, some disappointment has resulted from developments which were very promising in the beginning, but proved unsatisfactory both to the user and the miner. The matter of preliminary clay testing has been practically disregarded entirely, excepting by several well-established firms, and the cost of experimenting in the use of these clays devolved almost entirely upon the user, who in most cases was able to do this only by making up ware, a method of testing which is expensive, to say the least. A few easily made preliminary clay tests would have saved much time, money, and disappointment, inasmuch as they would have eliminated the most undesirable materials.

## Part II—THE USE OF BOND CLAYS IN THE MAKING OF GRAPHITE CRUCIBLES AND GLASS REFRACTORIES

### I. GRAPHITE CRUCIBLES

1. *Graphite.*—The graphite crucibles used in the melting of brass, steel, and various alloys consist, essentially, of a mixture of graphite and clay, which is shaped, dried, and fired to a moderate temperature usually at or below 800° C. The properties of the graphite which render it so valuable in connection with this use are its refractoriness, which to a certain extent is imparted to the clay bond, its reducing effect, which prevents oxidation of the metal, and its high thermal conductivity, which makes possible rapid fusion of the charge. In addition, the smoothness of surface which it imparts to the crucible permits the clean pouring of the metal.

The function of the clay is that of a bonding material, which makes possible the shaping of the crucible and the cementing together of the graphite flakes. At the same time, it covers the particles, and thus protects them from oxidation. In order to be most effective in regard to this point, it is necessary that the clay

contract and become dense at as low a temperature as is consistent with the required refractoriness.

The manufacture of graphite crucibles consists in thoroughly grinding together and blending the graphite and clay, tempering with water in a suitable mixing machine till the mass has assumed the proper plastic consistency, shaping the crucibles by means of a pottery jolly, drying, and finally burning them.

It might be well to consider somewhat in detail the two essential raw materials, the graphite and the clay.

The modification of carbon known as graphite has been defined as that allotropic form which has a specific gravity of from 2.25 to 2.26. Certain chemical tests, such as that of Brodie, consisting in treating the graphite with fuming nitric acid and potassium chlorate, have been employed to differentiate it from other forms of carbon, though with variable success. Arsem[2] states that lampblack heated to a high temperature in the electric furnace, possessing none of the characteristic properties of graphite, yielded the yellow graphitic acid of Brodie's test, though the specific gravity was only 2.122.

As to the real nature of graphite we are still in the dark. It is crystalline, rhombohedral, and stable at the highest temperatures. Its great softness, flaky structure, and feeble metallic luster are characteristic. Its specific heat varies in the natural and artificial varieties and according to the purity of the materials. Values have been determined for Ceylon graphite of from 0.174 to 0.2019 and for blast-furnace graphite of from 0.166 to 0.1970. The specific heat increases with temperature and has been found to be 0.467 at 977° C. The coefficient of thermal conductivity of graphite (gram calories through 1 cm cube) is 0.0141, and hence five times that of burned clay. The linear coefficient of expansion is 0.00000786 at 40° C. The excellent electrical conductivity of graphite is well known, but is not of interest in this connection.

Graphite occurs in nature in several forms, more or less admixed with impurities. It occurs in the older crystalline rock, gneiss, schist, crystalline limestone, granite, and sometimes in carbonaceous shales and slates. Though often occurring in small flakes throughout schist, as in Alabama, it is also found in veinlike deposits of considerable thickness. Of this character are the occurrences in the Laurentian rocks of New York and Canada, the graphitic gneisses of the Eastern Alps, the granulites of Ceylon,

[2] Trans. Am. Electro-Chem. Soc.; 1911.

and the granites in Irkutsk, Siberia. Massive graphite occurs also in Sonora district, Mexico, at Borrowdale, Cumberland (England), Passau (Bavaria), Schwarzbach (Bohemia), in Portugal, on the island of Madagascar, and in the Province of Minas Geraes (Brazil). The Mexican graphite mines are considered the richest in the world. In point of quality for the manufacture of crucibles the Ceylon graphite is considered the best, and enormous quantities are exported from there to Europe and the United States. In this country the best-known deposit occurs at Ticonderoga, N. Y., but a large number of ocurrences are to be met with in a number of States, as in Alabama, California, Pennsylvania, Georgia, North Carolina, New Hampshire, Rhode Island, Montana, and Virginia. Canada likewise possesses extensive graphite deposits. Large developments are under way at the present time in Alabama. In most American deposits the graphite occurs in small flakes interspersed in mica schist or similar rocks. The content of graphite scarcely ever exceeds 8 per cent, and it must be removed from the rocks by means of the usual methods of ore dressing. Of late oil flotation processes and electrostatic separation have been adopted successfully. As a rule, the domestic graphite is not as massive as the Ceylon product, consisting either of small flakes or, on the other hand, being more of a granular, amorphous character. The Ceylon graphite possesses to a marked degree a characteristic foliated structure combined with a low content of ash. Graphites differ widely in composition, and considerable variation is even observed in the Ceylon material. The purest grade of Ceylon graphite has been found to contain 98.87 per cent carbon, 0.90 per cent volatile matter, and 0.28 per cent ash. Frequently, however, shipments show a carbon content of 79.4 per cent and 15.5 per cent ash. In all graphites used for crucibles the ash content is of considerable importance, especially with reference to the amount of iron oxide present. If this constituent is too high it is apt to cause more rapid corrosion of the crucibles. Graphites have been examined in this laboratory which contain as high as 40 per cent of ash and 10 per cent of iron oxide. For the manufacture of graphite crucibles the Ceylon chip and flake graphite has been proven by years of practical experience to be exceedingly valuable. There is no reason, however, why Alabama graphite should not be used in admixture with the Ceylon product, or altogether for crucibles of the smaller dimensions, stoppers, and other accessories. The Ceylon graphite has an advantage in that it is of greater density,

which imparts to it greater resistance to oxidation. Its foliated structure and the possibility of sizing it to any desired series of grades, especially the coarser ones, cause the graphite-clay mixture to be more easily worked where large-sized objects are involved.

The fact that most domestic graphites are comparatively fine and of more uniform grain causes them to require more clay for bonding. To some extent this point is expressed by the volume occupied by unit weight of the different types of graphite. Thus, 100 grams of crushed Ceylon graphite, after thorough shaking, occupies a volume of 90.7 cc, Alabama graphite 152.0 cc, and Canadian graphite 119.6 cc, all three grades having been reduced to approximately the same size. This would tend to show that with the use of the maximum amount of American graphite bonded with clay, so as to be still workable, the carbon content would be smaller than when Ceylon graphite is employed. From this it follows that the ultimate density and thermal conductivity would be lower.

It is a fact that even with Ceylon graphite the sizing of the particles is of considerable importance, especially for crucibles used in the melting of steel, where it is desirable that the clay content be reduced to the minimum without impairing the density and strength of the product. This condition requires that the surface factor of the graphite be not too large, so that a relatively small amount of clay will suffice to cover and cement together the grains of graphite.

The computation of the surface factor may be illustrated by means of an example. A mechanical analysis was made of Ceylon graphite prepared by a commercial crucible plant and the dimensions of the particles determined by means of the micrometer microscope with the following result:

TABLE 3

| Tyler sieve | Residue left on sieve, per cent by weight | Average dimensions of particles | | | Average surface area of particle | Surface factor = 1 + average surface area |
|---|---|---|---|---|---|---|
| | | Length | Breadth | Thick-Thickness | | |
| | | mm | mm | mm | mm² | |
| On 20-mesh | 30.30 | 2.06 | 0.92 | 0.272 | 5.4000 | 0.185 |
| On 40-mesh | 45.20 | .96 | .75 | .111 | 1.8160 | .550 |
| On 80-mesh | 18.34 | .49 | .35 | .0457 | .4190 | 2.386 |
| On 100-mesh | 2.19 | .30 | .214 | .0252 | .1543 | 6.480 |
| Through 100-mesh | 3.97 | .12 | .075 | .02025 | .258 | 38.76 |

Multiplying the percentages of the different sizes by their respective surface factors and adding, we obtain:

$$30.30 \times 0.185 + 45.20 \times 0.550 + 18.34 \times 2.386 + 2.19 \times 6.480 + 3.97 \times 38.76 = 88.06$$

as the surface factor of the graphite mixture. It will be noted that the surface factor increases very rapidly with the finer sizes. For this reason the amount of fine material must be regulated and kept as constant as possible for the same kind of work.

The purification of graphite, too high in ash content, by chemical means such as treatment with hot caustic-soda solution followed by washing with diluted acid, or with acid alone, has been carried on successfully in the preparation of graphite for the lead-pencil industry, but apparently is too expensive for crucible graphite. At the same time, such treatment requires fine grinding, which is not desirable for the purpose under discussion. It is interesting to note, however, that it has been possible to produce practically an ash-free product from graphite containing 11 per cent of mineral matter. The content of iron oxide may be reduced very largely by exposing the graphite to a current of chlorine gas at a temperature of approximately 600° C.

The simplest tests for the purity of graphite are the determination of its specific gravity and of the ash content.

The apparent specific gravity of American flake graphite was found to be 2.35, of Ceylon 2.36 to 2.43. There is, however, a variation in density according to the size of grain.

2. *Artificially Prepared Graphite and Carbon.*—Upon heating anthracite or coke to a high temperature in the electric furnace the carbon is converted into graphite. This transformation is practically complete and may result in as much as 99 per cent graphite. Owing to the great demand for artificial graphite for electrodes, lubricating, and other purposes, this material, from the standpoint of cost, is not available for crucible making. At the same time, its structure is not as desirable as that of the natural graphite, and its rate of oxidation under furnace conditions is appreciably greater. Graphite is formed also by segregation from cooling metal, as in the case of blast-furnace iron. Large quantities of scalelike graphite, known as "kish," are thus produced. The lamellæ of this type of graphite are exceedingly thin and fragile, and in incorporating a given weight of this material in clay much more of the latter and of water is required than when natural graphite is employed. Blast-furnace graphite, as a rule, contains a good deal of iron, which would make necessary purifi-

cation by means of an acid treatment. This type of graphite oxidizes more readily than natural graphite, and is also more readily absorbed by molten steel.

Sources of noncrystalline carbon are also coke, retort graphite formed in gas retorts, and the carbon resulting from the decomposition of hydrocarbons.

In European practice both coke and retort graphite have been admixed with the natural graphite for making crucibles. The practice is not desirable for steel melting, since the amorphous forms of carbon are more soluble in the molten metal than crystallized graphite, and hence cause too much cementation. Their more rapid rate of oxidation is likewise detrimental for this purpose.

Some of the Birmingham crucibles are said to be made up of 3 parts (by weight) of graphite, 2 of hard coke, 2 of Stourbridge clay, and 1 of ground sherds from old crucbles. Crucibles used in a Germany foundry have been made from a mixture consisting of 5 parts of ground coke, 4 of graphite, and 8 of Stourbridge clay and grog. If the necessity arose, it would be, of course, possible to use crucibles in which all the carbon is introduced in the form of retort carbon, coke, or electric-furnace graphite, even though the results were not as satisfactory as those obtained with the natural graphite.

It might be interesting to note that in melting an alloy of 68 per cent copper and 32 per cent zinc in a No. 60 crucible consisting of 50 per cent blast-furnace graphite, 6.75 per cent Maryland plastic bond clay, 12.5 per cent clay from Anna, Ill., 6.25 per cent Laclede-Christy bond clay, 12.5 per cent Kentucky ball clay, and 12.5 per cent siliceous bond clay from Lester, Ark., 25 melts were obtained. Considering the type of graphite and the high clay contents this is a very good showing.

In using electric furnace graphite an average life of 17 melts of the alloy given above were obtained from the two mixtures:

| | Per cent | |
|---|---|---|
| Electric furnace graphite | 55 | 60 |
| Plastic clay from Laurel, Md | 6 | 5 |
| Plastic clay from Anna, Ill | 10 | 10 |
| Plastic clay, St. Louis, Mo | 10 | 5 |
| Ball clay, Mayfield, Ky | 10 | 10 |
| Plastic clay, Lester, Ark | 9 | 10 |
| | 100 | 100 |

3. *Crucible Mixtures.*—As has been pointed out in previous paragraphs, the main requirements of a suitable crucible mixture are that it must possess satisfactory working qualities, good strength in the dried state, ability to withstand sudden temperature changes, good thermal conductivity, freedom from pinholes, sufficient mechanical strengh to stand up under rough treatment with tongs, and slow oxidation of the graphite.

The clays most desirable for this purpose are those of the dense-burning type, which soften slightly at the heat of the brass furnace. The open-burning clays are not suitable for this purpose, though they may be used for the purpose of stiffening clays deficient in refractoriness. The amount of kaolin and other open-firing clays thus used must not ordinarily exceed 10 per cent. The clays to be considered here are those of the Klingenberg type; some of the English ball clays, such as that marketed as "Dorset;" the ball clays from Mayfield, Ky., and the Paris, Tenn., district; the bonding clay mixtures marketed at St. Louis, Mo.; the plastic bond clays from northern Mississippi, from near Portsmouth, Ohio, Laurel, Md., and Anna, Ill. The properties of these types of clays have already been discussed in detail in the preceding section. In every case those clays are to be preferred which vitrify close to 1150° C.

The compositions of graphite crucibles vary considerably with reference to whether they are to be used for brass or for steel melting. Some of the mixtures which have come to the knowledge of the writer are as follows: the first four being principally intended for melting brass and the last two for steel:

TABLE 4

| | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| Graphite | 48 | 57.5 | 55 | 50 | 58 | 55 |
| Bond clay | 32 | 25.5 | 35 | 40 | 35 | 30 |
| Kaolin, plastic | 6 | 10.4 | 5 | ..... | ..... | 7 |
| Sand | ..... | ..... | ..... | 5 | 7 | 8 |
| Crushed pot shell | 14 | ..... | 5 | 5 | ..... | ..... |
| Potter's flint | ..... | 6.6 | ..... | ..... | ..... | ..... |

The addition of sand can be avoided by the use of a siliceous clay, like that from Arkansas (Lester), which makes possible a reduction of the clay content, if this is desirable, and yet the maintenance of good working quality. In making up crucibles with

55 per cent of chip and flake graphite good results have been obtained by the use of 8 per cent of sand and 37 per cent of a mixture of Maryland, Illinois, Missouri, and Kentucky clays, approximately in equal parts. Upon introducing Arkansas clay, which is very siliceous, no sand addition was found necessary, and the five clays were used in the proportion of 9 per cent each, thus making possible the use of more graphite or the partial substitution of flake for Ceylon graphite. The Mississippi clays have been found to be especially well suited for crucible making, and the large deposit available makes them a promising source of supply. As has been pointed out before, the blending of several clays is desirable for securing that combination of properties most satisfactory for the purpose. This makes it possible to arrive at a combination even more efficient than the use of the imported clay. At the same time, there would be less difficulty due to the unavoidable variations invariably met with in the mining of a single clay, since it is extremely improbable that all of the clays of the mixture should vary in the same direction at the same time. In making mixtures of any kind it is essential that the clays be blended intimately by mill grinding; otherwise the best results can not be obtained. The clay question should then resolve itself into the use of from two to four clays, which should constitute the standard batch and which should not be changed except for good reasons. Deficiency in refractoriness can be corrected by the use of kaolin; lack of density or insufficient vitrification by the use of a tight firing plastic clay, higher in fluxes; and inability to resist the pressure of the molten metal, as evidenced by the bulging of the crucible, by the addition of quartz.

For the purpose of securing data concerning the relative resistance to oxidation offered by mixtures composed of Ceylon graphite and clay in the proportion of 1:1, specimens were molded in the form of open cubical boxes measuring 3¾ inches outside and 2⅜ inches inside, thus having walls ⅛ inches thick. These were pressed in the plastic state, dried, inclosed in saggers containing coke, and fired in a kiln, to a temperature of 1125° C. The burnt specimens were then reheated in a muffle under decidedly oxidizing conditions at 1000° C. Every hour a specimen was withdrawn, cooled, and weighed. The loss of carbon due to oxidation was thus determined for each clay-graphite mixture. The results are compiled in Table 5.

TABLE 5

| Bond clay | Porosity of clay at 1125° C | Per cent loss in weight, in terms of original weight, after oxidation at 1000° C continued for— | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 hour | 2 hours | 3 hours | 5 hours | 9 hours | 17 hours | 23 hours |
| | Per cent | | | | | | | |
| English ball clay | 2.47 | 2.77 | 5.94 | 7.75 | 9.09 | 12.85 | 19.27 | 20.84 |
| Southern Illinois clay | 26.27 | 4.52 | 7.37 | 9.92 | 12.62 | 15.70 | 24.18 | 26.92 |
| Tennessee ball clay | 18.85 | 3.21 | 7.29 | 9.06 | 10.91 | 17.05 | 22.35 | 29.42 |
| Klingenberg | 3.80 | 3.77 | 8.63 | 10.30 | 11.80 | 17.67 | 25.72 | 30.20 |
| Maryland | 17.13 | 3.84 | 8.65 | 9.20 | 13.50 | 18.60 | 29.60 | 31.40 |
| Kentucky | 20.26 | 4.11 | 8.22 | 11.82 | 15.12 | 18.87 | 27.15 | 33.15 |
| Missouri | 17.85 | 5.19 | 9.19 | 11.50 | 13.96 | 19.44 | 31.02 | 34.25 |
| Southern Ohio | 19.15 | 5.18 | 11.35 | 11.05 | 15.00 | 22.80 | 31.75 | 34.60 |
| Tennessee ball clay | 19.03 | 4.00 | 9.65 | 12.80 | 15.20 | 24.30 | 30.40 | 36.70 |
| Do | 38.00 | 6.30 | 11.18 | 11.35 | 14.70 | 21.45 | 33.50 | 39.60 |

From these it follows that the Klingenberg clay is by no means the most protective material and is excelled in this respect by three other clays. On the other hand, the losses in weight are not as conclusive as might be desired, and seem to bear no close relation to the porosity as might be expected. The variation in loss due to oxidation does not fluctuate within wide limits. The outstanding fact is that low porosity, while certain to bring about some protective action, is not the sole factor involved.

An interesting fact, developed in some work done in this laboratory in the treatment of clays, might be promising from the commercial standpoint. In grinding soft lignite with water the latter assumed a dark-brown color, due to the suspension of very fine particles of carbonaceous matter. By using this liquid in place of the ordinary water, taking care to screen out all particles not passing the 120-mesh sieve, the bonding quality and toughness of the clay seems to be improved to an appreciable extent. This is somewhat analogous to the well-known process of Acheson, depending upon the use of tannic acid to improve the plasticity of clays, but does not have the bad effects of this reagent in the drying of the clay.

4. *Manufacture and Use of Crucibles.*—The preparation of the graphite consists usually in grinding it by means of a buhrstone mill or pan or disintegrator and sizing it by means of sieves. But a small amount of the dust is used, which is frequently utilized for nozzles, stoppers, and other articles. The sized mineral is usually stored in bins, from which it is weighed out in the proper proportions, together with the ground-clay mixture. The materials are then mixed together in the dry state, avoiding further grinding,

for which purpose a kneading machine may be employed. As soon as the dry mixing is completed water is added and the tempering continued until the soft plastic state has been attained and the whole mass is of uniform consistency throughout. The material is then allowed to cure or age for some time in the clay cellar. The crucibles are molded by means of the potters' jolly in plaster or metal molds lined with cloth. As regards to drying, the usual pottery practice is followed. The application of the modern humidity-drying methods, at least for the larger crucibles, should offer an opportunity for improvement, since uniformity of shrinkage is not always secured under the present conditions.

The firing of the crucibles is carried to a temperature but little above the temperature of complete dehydration of the clay, usually between 650 to 700° C. Even in muffle kilns some loss of graphite occurs on the surface of the crucibles through oxidation, as is evidenced by the white coating of clay. It would be presumptuous to say that we understand all the factors entering into the construction of the crucible body, nor do we understand clearly the various destructive agencies tending to shorten the life of crucibles.

It is obvious that laboratory work along these lines is difficult to carry on without having access to a crucible plant, as the question of workmanship enters vitally into the testing of the different mixtures. Much is yet to be learned. It is believed, however, that the future will show that the application of ceramic principles, so extensively applied in the production of porcelain and other clay products, are of service also in this connection. The American manufacturers of crucibles have been confronted by a serious situation, and they have done well under the circumstances, rendered especially difficult by the prevailing strenuous industrial conditions. Whether or not American crucible makers will return to the use of the Klingenberg clay remains to be seen.

It is quite apparent to the casual observer that the treatment to which graphite crucibles are subjected is often extraordinarily severe. In the first place it is doubtful whether the function of drying out the crucibles is properly understood. Graphite crucibles are not fired to a high initial temperature and hence retain a porous structure. In common with all other clay products not burned to vitrification the crucibles are hygroscopic; that is, they greedily absorb moisture from the atmosphere, which is more difficult to expel than we generally realize.

Low-fired clays differ widely as to their hygroscopic capacity and the temperature at which they release the moisture thus absorbed. At the same time, the expulsion of this moisture requires considerable time. Therefore, it is not sufficient simply to keep the crucibles in a warm place, but they should be finally maintained for at least several days at a higher temperature, say 150° C before being placed in the furnace. In Europe the crucibles on being taken from this kiln are sometimes covered with a waterproof coat, such as tar or pitch dissolved in turpentine.

The preheating of the crucible just before putting into the heat for the first time, likewise, is often too abrupt, and hence the temperature change to which they are subjected too violent. The ideal method of handling the fresh crucibles would be to place them in a special furnace kept heated by the waste gases of the melting furnace, where the temperature could be brought up uniformly to somewhat below red heat.

The conditions of heating are of great importance. It is evident that the intense heat of an oil burner will bring a large crucible far closer to the softening point than when it is exposed to the fire of a coke furnace. The larger the crucible and the higher the level of the liquid metal, the lower in temperature must be the failing point of the crucible, since at furnace temperatures even comparatively small loads tend to bring about deformation. Add to these factors the effects of unequal heating and rough handling, and it can readily be seen why the life of crucibles varies so widely.

## II. GLASS WORKS REFRACTORIES

1. *Pot Mixtures.*—It has been assumed by American glass manufacturers that the refractories used by them, glass pots, tank blocks, floaters, boots, etc., for best results require the use of German clay, principally that obtained at Grossalmerode, the properties of which are discussed in the preceding section. The fact that this clay possesses good plasticity, safe drying qualities, low drying and low fire shrinkage, and at the same time, owing to its siliceous nature, resists the action of the commercial glasses very satisfactorily, has made it a standard raw material. The low temperatures employed in American pot arches have required the use of clays of low fire shrinkage, since evidently it is not admissible to permit the contraction taking place in the melting furnace to be too great, owing to the severe stresses to which the pots would be subjected.

Refractories for the glass industry are made, as a rule, from a mixture of calcined clay, consisting partly of crushed old pot material, carefully cleaned, and plastic bond clay. The proportion of calcined (grog) to plastic clay usually is between 1:1 to 3:2. In some glass plants no clay but the Grossalmerode material and pot shell was used; in others the plastic clay from Missouri was introduced, and, again, in some cases a smaller amount of raw flint clay was added. Some of these mixtures are as follows:

TABLE 6

| Clay | a | b | c | d |
|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent |
| Grossalmerode clay, raw | 47.0 | 20 | 24 | 25 |
| Grossalmerode clay, burnt | ..... | 10 | ..... | ..... |
| Missouri plastic clay, raw | ..... | 20 | 16 | 20 |
| Missouri clay, burnt | 26.5 | ..... | 15 | 15 |
| Flint clay, raw | ..... | ..... | 15 | 10 |
| Pot shell | 26.5 | 50 | 30 | 30 |

These mixtures, taken as a whole, gave satisfactory results with the usual soda-lime glasses. It was taken for granted that the pots and tank blocks would have about so long a life, and it was also assumed, as a matter of course, that they would not last so long with lead or special glasses. The considerable, though uniform, solution of the refractories due to the presence of the siliceous German clay was not thought objectionable. The results were not so good when the proportion of the Grossalmerode clay was above the average, and especially in the case of the more corrosive glasses. In general, it was not realized that different refractories are required for different types of glasses, and unfortunately no special efforts were made, excepting by one or two large companies, to improve matters. With the outbreak of the war and the elimination of the German clay more or less confusion occurred, and the exclusive use of domestic clays was not always successful, for reasons which will be considered later. A search was made for substitutes, with the result that a number of new clays were brought on the market, and the mining operations of the well-known and reliable Missouri clays from the St. Louis district enlarged. Among the clays brought forward in this connection were the ball clays of Tennessee and Kentucky, already used to a large extent in the pottery and tile industries, the siliceous clay from Lester, Ark., the plastic fire clays from near Ports-

mouth, Ohio, and the clays from southern Illinois. The physical properties of these clays have already been discussed. The Arkansas clay was found to be very similar to that from Grossalmerode, but it required to be supplemented by a plastic, more aluminous clay, firing to a dense structure at a lower temperature, approximately 1250° C. For certain glasses satisfactory results have been obtained with the use of only the Missouri washed plastic clays in the raw and burned state, employing in addition about 10 per cent of calcined flint clay. In other cases, using some of the other clays mentioned, unsatisfactory results have been obtained, due principally to cracking of the pots around the bottom. The resistance of the American clays to corrosion has usually been very satisfactory and better than that of the German clay. The cracking must be ascribed merely to the greater firing shrinkage of the American clays.

2. *Fire shrinkage.*—The maximum temperatures of our pot arches are usually very low, to say nothing of their extreme irregularity. Rarely do they exceed 1000° C, which is entirely insufficient to cause more than a slight amount of heat contraction. The bulk of the shrinkage remains to be accomplished in the melting furnace under the most adverse conditions due to unequal heating and under the pressure of the glass charge.

The differences in contraction of the different clays are shown in the following table:

**TABLE 7.—Contraction of Bond Clays**

| Clay | Drying shrinkage, in per cent of dry volume | Firing shrinkage, in per cent of volume in dried state, at temperatures of— | | | | |
|---|---|---|---|---|---|---|
| | | 1050° C | 1100° C | 1200° C | 1290° C | 1400° C |
| Grossalmerode | 20.57 | ..... | 4.14 | 7.84 | 8.55 | 10.70 |
| St. Louis district | 28.52 | 8.70 | 13.62 | 19.60 | 23.25 | 24.35 |
| Tennessee ball clay | 29.51 | 17.90 | 32.20 | 39.12 | 42.75 | 38.45 |
| Kentucky ball clay | 34.53 | 11.49 | 26.80 | 37.01 | 41.75 | 39.55 |
| Southern Ohio, washed | 40.61 | 7.08 | 14.50 | 20.20 | 26.02 | 25.41 |

These figures show the point brought out with unmistakable clearness. It will be noted that the fire shrinkage of the German clay is far less than that of the American bond clays. Assuming that the mean pot arch temperature is 1050° C, which is above the point usually reached, and that the mean furnace temperature is 1290° C, the Grossalmerode clay will contract about 7 per cent of the dry volume; the St. Louis clay, 14.55; the Tennessee ball

clay, 24.85; the Kentucky ball clay, 30.26; and the Ohio material, 18.94 per cent. Thus, allowing for a grog content of 50 per cent, the contraction in the furnace of a pot having a solid content of 10 cubic feet would vary from 0.75 to 1.5 cubic feet of displacement, a condition which taxes the strength of the body to the limit. The figures given show also one reason why the Missouri clays have been preferred for pot making, their fire shrinkage being the lowest of the American clays cited. It is evident, therefore, that the use of a siliceous clay like that from Arkansas with a fire shrinkage of only 1.6 per cent at 1290° C is greatly to be desired. Its exclusive use, however, is not desirable, as has been already stated, due to its too open structure, and its combination with a clay of the ball clay type should prove eminently satisfactory. The proper admixture can be approximately computed from the values given in the tables of Part I, both on the basis of shrinkage and desired density at the furnace temperature in question.

The large furnace shrinkage of American bond clays may be overcome by admixture with a siliceous clay or sand, by increasing the content of grog or by sizing,[4] the latter to yield mixtures of minimum shrinkage (increasing the fines), and by the employment of higher pot-arch furnaces.

The use of siliceous clays probably offers the easiest remedy, since materials of this type are plentiful and are to be found in large quantities in New Jersey, as well as associated with many of the fire-clay deposits of Missouri, Kentucky, Tennessee, Ohio, Pennsylvania, and other States. It is not desirable to reduce the shrinkage of the clay or the pot body to its lowest possible value; but the fire contraction of the blended clay mixture (without grog) should be about 12 to 15 per cent, in terms of the dry volume, at 1300° C. It is obvious that exact limits can not be given to cover all cases. The introduction of more siliceous clay than is necessary to reduce the pot contraction to a value consistent with safe operation (freedom from fire cracks) is not desirable, since the rate of corrosion may become too great, especially in the case of flint glasses. Furthermore, the danger of fire checking due to the presence of too much free quartz is a distinct danger which is to be avoided. The exclusive use of Grossalmerode clay frequently has lead to this difficulty in the past, and from old records it has been learned that often such pots are considered "tender."

[4] Bureau of Standards Tech. Paper No. 104.

Chemical analysis is useful in checking the silica content of mixtures. It is evident that if in a clay mixture a silica content of 62 per cent is to be maintained and clays a and b contain 80 and 51 per cent silica, respectively, they must be blended in the proportion of 11:18.

For purposes of comparison an average analysis of Grossalmerode clay is given herewith:

| | Per cent |
|---|---|
| Silica | 73.08 |
| Alumina | 15.75 |
| Titanium oxide | 2.10 |
| Ferric oxide | .62 |
| Lime | .54 |
| Magnesia | .33 |
| Potash | .27 |
| Soda | .16 |
| Loss on ignition | 7.11 |
| Mineral composition: | |
| Clay substance | 44.28 |
| Quartz | 53.03 |
| Feldspar | 2.69 |

3. *Porosity and Refractoriness.*—It is desirable that the porosity of the pot body be as low as possible when the glass charge is introduced, though it must be realized that this requirement is somewhat contradictory to the other condition, namely, that the fire shrinkage be low also. However, a compromise may be reached by employing with the siliceous clay a material burning dense at the furnace temperature. Thus the Grossalmerode clay has a porosity of 16.9 per cent at 1290° C, while the St. Louis district shows only 8.96 per cent. A combination of the two results in a value which is midway between these figures.

It is evident, again, that the Arkansas clay, having a porosity of 25.6 per cent at the above temperature, requires a larger amount of dense-burning clay to reach the desired degree of compactness. If to the siliceous material a clay could be added possessing a still lower porosity at the temperature mentioned, this would be a further improvement, providing, of course, that the refractoriness of the mixture was not lowered below the permissible boundary. Deficiency in refractoriness may be made up by the addition of kaolin or flint clay.

It is necessary to realize the fact that siliceous clays are more sensitive to the presence of fluxes than the more aluminous ones, and hence it is quite possible that by the admixture of a material of the first type with one of the second which is somewhat high in

fluxes, a complex eutectic may be formed, which causes the refractoriness to become too low.

Attention might be called also to the fact that careful drying of glass pots and tank blocks is essential, since not infrequently damage done by too rapid or irregular drying manifests itself when the pot has been placed in the melting furnace. The application of the humidity-drying systems promises to offer a solution of the difficulty in insuring safer drying conditions both as to temperature and steady drop in the vapor pressure of the moist air surrounding the objects to be dried.

4. *Preheating.*—It would seem most desirable also to depart from the old construction of the pot arches, which may be adquate for the smaller pots used formerly, but do not serve the purpose of preheating the large sizes commonly employed at the present time.

Temperature readings observed in arches show exceedingly wide variations between the top and bottom of pots. The bottom, subject to the most intense corrosive action of the batch, is usually underfired. The result is that the difference in shrinkage between the several parts brings about a severe stress, apt to lead to cracking, and at the same time the porous structure of the bottom leads to destructive corrosion.

It would seem desirable to abandon the present pot-arch construction entirely and to adopt either the down-draft or the up-draft firing so commonly used in the clay industries. It is likewise to be recommended that the firing be done from two sides, over bag walls, very similar to the arrangement of the rectangular down-draft kiln employed in brick burning. By the use of a perforated kiln bottom the heat and flames may be directed at will and can be caused to surround the bottom of the pots which are placed on blocks, thus insuring proper burning of this part. The use of either the down or up draft firing, provided ample draft is available, makes it possible to preheat the pots to a higher temperature, say 1200 to 1300° C. The result will be that the maximum amount of fire shrinkage will be accomplished where it should be and not left to be done in the melting furnace. The use of very siliceous clays then becomes no longer necessary, and more aluminous, denser materials may be employed which show better resistance to corrosion, especially in the melting of flint glasses.

Too little attention is given also to the heating up of pots and tank blocks. Much time is often consumed unnecessarily in the first heating while the dehydration and oxidation range,

500 to 800° C, is frequently passed too rapidly, resulting in permanent damage to the pots. Well considered heating schedules should be adopted, which result in a perfectly oxidized and sound structure. While this precaution is not of such great importance in the use of Grossalmerode clay, it becomes imperative when the denser American clays are used, since these nearly always contain more or less carbonaceous matter. The time required for passing through the range between 500 to 800° C may be determined with accuracy by firing with the pots a number of cubical blocks made of the same mixture, measuring say, 4 or 5 inches. Upon removing one of these specimens from time to time and breaking it the fracture should be of a light, uniform color, free from any gray or dark area in the center. The temperature must not be allowed to exceed 800° C until the dark core has disappeared and a block when drawn and split has the desired appearance. In this manner the rate of heating the arch may be established once and for all for a given pot composition. The time thus lost by holding within the temperature limits given may be regained by firing quite fast from this point to the maximum temperature, as no damage can be done. It is desirable, however, to hold the final temperature until the contents of the arch have been uniformly heated throughout. Such a firing schedule need not require more time than is being consumed by the old practice.

It is true that in using down-draft arches a stronger draft will be required, but a stack 50 feet high should be ample for the purpose. The regulation of the draft by means of a flue damper is necessary and will result in saving of fuel.

It is not improbable that the pot arch of the future will be of the continuous-tunnel type, in which the pots are placed and fired on cars similar to the kiln already employed in some of the clay industries.

What has been said of glass pots applies in general to tank blocks. In these the importance of a sound molding structure and of uniform firing to a fairly dense structure is even greater, owing to the heavy cost involved in cooling down a tank furnace. It is very probable that in the future the hand molding of blocks will be replaced by pressing on a large auger machine or piston press to prevent the structural irregularities so difficult to avoid in hand work. It is necessary also that more attention be paid to the thorough oxidation and more complete burning of the blocks.

### III. SPECIAL POTS FOR THE MELTING OF OPTICAL GLASS

1. *Semiporcelain and porcelain pots.*—It was realized at the very initiation of the work on optical glass, begun in the Pittsburgh laboratory of the Bureau of Standards about five years ago, that the production of suitable pots plays an important part in the manufacture of this type of glass. It is evident that the pot material must resist corrosion by the glasses, some of which are very active in this respect. The solution of the clay body in the glass causes serious difficulty through the production of striæ due to disturbance of the homogeneity, resulting in threads or strings which are stirred into the molten mass. It should be stated here, however, that solution of the pot is not the only cause of striæ, but that they may be due to lack of homogeneity in the glass itself. Again, it has been observed that the constituent of the pot body first dissolved by the glass is iron oxide. The coloring power of iron, especially with the heavy flint and barium glasses, is very intense, so that very small quantities suffice to impart to the melt a very decided yellow or green shade. This coloration is injurious not only for optical reasons with reference to photographic purposes, but it is a powerful factor in cutting down the light transmission. Since the use of decolorizers is out of the question in optical glass, owing to the high absorption of light caused by them, it is obvious that the content of iron oxide must be kept down by the use of practically pure reagents and by the use of pots as low in this constituent as possible. It will be readily seen that by the use of the ordinary type of pot the amount of iron brought into the solution might easily be several times that of the original iron content of the entire glass batch. The use of even the purest reagents would thus be of no avail.

It would appear that pots used for this purpose should be resistant to corrosion by the molten glass, yet sufficiently refractory to withstand the high temperature of the furnace, which may approach 1475° C, and the hydrostatic pressure of the liquid charge, and should be as low in iron oxide as possible. Since the pots are used but once, the thickness of the bottom and walls may be cut down to the minimum. Owing to the high value of the glass, the cost of the pot, within obvious limits, is not a serious consideration.

The first pot mixture used in this laboratory, when operations were begun on a larger scale, was as follows:

| | Per cent |
|---|---|
| Laclede-Christy bond clay, 69–B | 6 |
| Tennessee ball clay | 5 |
| Bond clay from Anna, Ill. | 7 |
| Kentucky ball clay | 5 |
| "Highlands" fire clay, St. Louis | 5 |
| North Carolina or Delaware kaolin | 12 |
| Calcined "Highlands" clay, 10-mesh | 20 |
| Calcined kaolin, through 16-mesh | 40 |
| | 100 |

In using this mixture it is necessary to calcine the kaolin to a temperature of not less than the softening point of cone 14. This, of course, increased the cost of the pots. Later, the calcined kaolin was replaced by a mixture of 80 per cent kaolin (North Carolina, Florida, and Georgia in equal parts), 10 per cent of flint, and 10 per cent of feldspar, fired also to cone 14. This gave a sharper and less friable grog. Both compositions gave excellent results with reference to the standing-up qualities and the resistance of the pots to corrosion. Still, the iron content of the mixture was somewhat too high, and it was thought desirable to work out a composition akin to that of a hard porcelain. After some experiments the following composition was arrived at:

| | Per cent |
|---|---|
| Calcine | 43 |
| Kaolin | 25 |
| Plastic bond clays | 25 |
| Feldspar | 7 |
| | 100 |

Here, the calcine consisted of the kaolin, feldspar, and flint mixture mentioned above. It is evident that in blending such a number of materials great care is necessary to secure thorough dry mixing and pugging. These pots likewise gave very satisfactory results.

The question of procuring the calcine in larger quantities was found to be an annoying one, and a cheaper source of grog was sought. This was found in the waste bisque of white-ware potteries, which is obtainable at a reasonable price and in sufficiently large quantities. This type of body corresponds to the general composition of 35 per cent kaolin, 15 per cent ball clay, 14 per cent feldspar, and 36 per cent flint. The white-granite bisque softens at about cone 30 and possesses, on account of the high flint content, excellent standing-up qualities under conditions of

pressure and at high temperatures. It is evident that porcelain bisque, whether tableware, electrical porcelain, or floor tile, would not answer for this purpose, owing to the low refractoriness. There would be no objection, of course, to the use of this kind of material in replacing the feldspar introduced, the proportions of white-ware bisque and porcelain bisque introduced being such as to maintain the desired refractoriness. In employing white-ware bisque it should be obtained in as clean a condition as possible, and care should be taken not to produce too large a percentage of fines (finer than 80-mesh) in grinding. If this grog should become too fine, it might cause serious cracking of the pots during cooling, probably at a temperature of about 625° C, when the glass is still in a semifluid condition. This defect is due to vitrification, facilitated by the presence of the fine particles of grog and the resulting homogeneous porcelain structure. In satisfactory pots the grains of grog should still retain their identity as shown by their outlines.

For some time both white-ware bisque and old pot shell (from porcelain-type pots) have been used, and the composition of the pot batch is as follows:

| | Per cent |
|---|---|
| White-ware bisque, through 10-mesh | 35 |
| Pot shell, through 10-mesh | 10 |
| Feldspar | 3 |
| Flint | 4 |
| Tennessee ball clay, No. 5 | 15 |
| Kentucky bond clay, No. 4 | 5 |
| Kaolin | 28 |
| | 100 |

The ground and screened grog and other components of the body batch are weighed, mixed, and then tempered in a wet pan. It is desirable in tempering that the mullers be raised about one-fourth inch off the bottom of the pan, so that the grinding action is reduced to the minimum. The clay is then passed through a vertical pug mill and stored as long as possible. The body should be aged at least a month. The treading of the plastic body has been discontinued. The pots are built up by hand in the usual manner, and both the open and covered types are made. The pot used in this laboratory is 34 inches in diameter (outside), 27 inches high, and has a bottom 4 inches thick. The wall tapers from 2½ inches (top) to 3½ inches (bottom). The weight of each pot is about 550 pounds. After drying for about four weeks the pots are ready for the furnace.

2. *The Casting of Pots.*—One or two pots each week are also being made by the casting process. The composition of this body is as follows:

| | Per cent |
|---|---|
| White-ware bisque | 48 |
| Plastic bond clay | 22 |
| Kaolin | 23.5 |
| Feldspar | 6.5 |
| | 100 |

The slip used carries 80 per cent of solids, and hence 20 per cent of water. A mixture of sodium silicate and sodium carbonate in the proportion of 4:3 is used as the electrolyte and the amount added, in terms of the dry weight of the body, is 0.20 per cent as the anhydrous salts. The arrangement of the mold, as shown in the illustration, Fig. 24, needs no detailed description. It is, of course, necessary to hold the core firmly in position by means of crossbeams and tie-rods, as the upward hydrostatic pressure of the slip is considerable. The casting, as now practiced, is through three funnels arranged symmetrically around the circumference of the mold. The liquid in the funnels is replenished as the level is lowered. During the last stage of the casting the settling is very slow, so that the funnels may be filled and the process allowed to go on without close supervision. Absorption of the liquid ceases after about 16 hours, and the core may then be removed. The outer mold may be removed after 24 hours. Suitable hoists are necessary for the handling of the mold parts and the pots.

The process of preparation of the slip is very simple, consisting in introducing the weighed, ground body constituents into a double blunger, together with the required amount of water in which the electrolytes have been dissolved. When the desired consistency has been attained, the slip is allowed to run into a large bucket, which is conveyed to the mold, hoisted, and the slip discharged into the funnels. No difficulty has been experienced in drying the cast pots in less than four weeks. They have given very good satisfaction in the glass furnaces and, if anything, are superior to the handmade ones, especially on account of the fact that they have thinner walls, the thickness varying from 2 to 3 inches. For this reason less time is required in the heating up period.

In the use of porcelain-type pots it is important to raise the temperature of the furnace to not less than 1400° C, before the charge is introduced, in order that the body may become vitri-

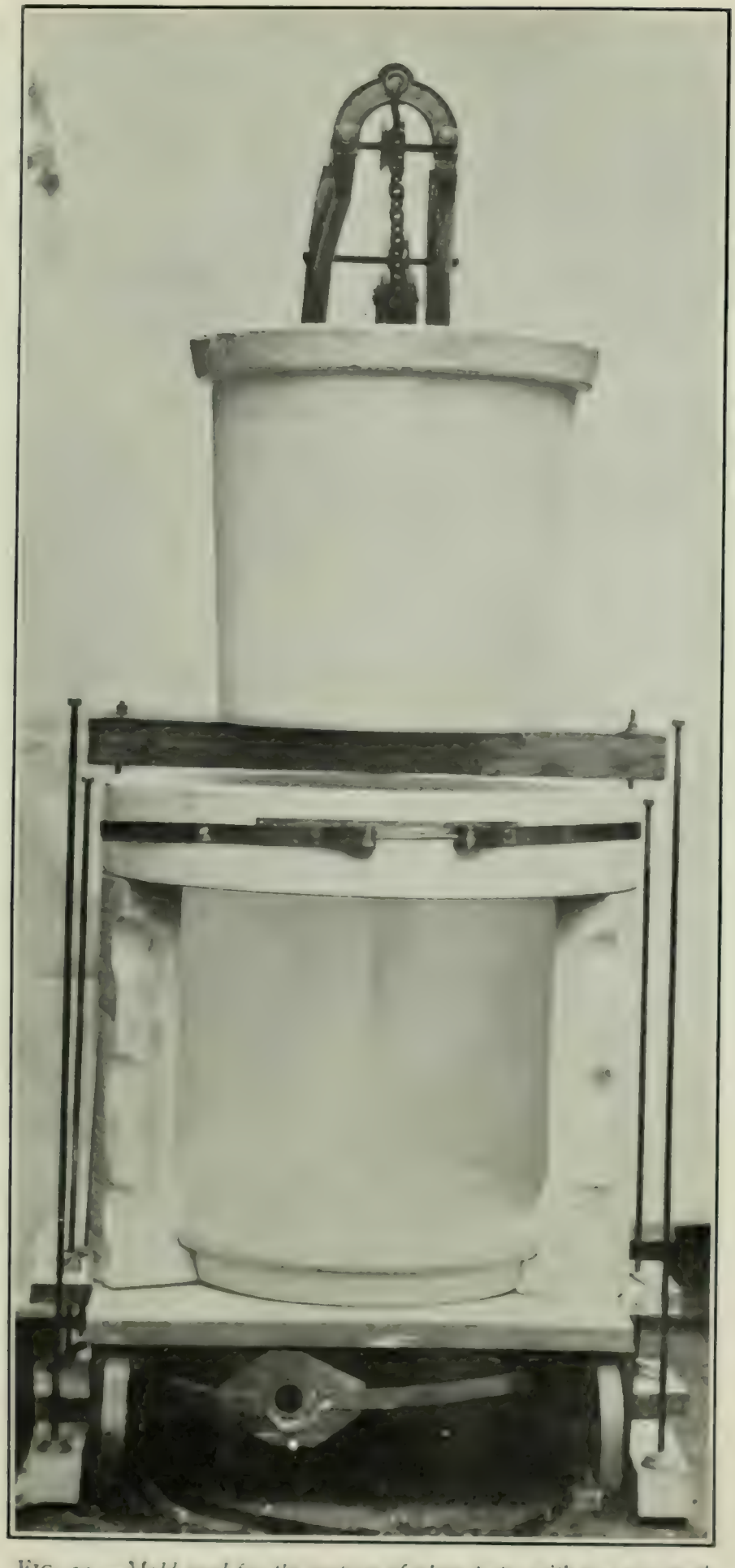

FIG. 24.—*Mold used for the casting of glass pots, with core removed*

fied. The temperature may then be lowered, and the glass batch introduced into the pot. Unless this is done the benefits of the porcelain structure are lost, and the pot may corrode as much or more than one of the ordinary type.

The same body composition is also used in the casting of the stirring-rod parts, which are immersed in the glass during the mixing stage of the melt.

## IV. SUMMARY

The physical properties of three typical German clays formerly imported in large quantities have been described in detail and on the basis of constants, which make possible accurate comparison and evaluation of American materials. Similarly, the physical characteristics of 23 American and 2 English bond clays have been determined. Of these several approach the Klingenberg and Grossalmerode clays quite closely. Others, by suitable blending, can be made to equal or excel the European clays.

For crucible making the best clays should show a pore-shrinkage water ratio of not more than 1:1; a modulus of rupture for a clay-sand mixture of 1:1 of about 325 pounds per square inch; a vitrification point of 1150° C, or lower; no marked evidence of overfiring at 1,400°, C; and a softening point corresponding to Orton cone 31, or above. For glass pots the best materials should show a pore-shrinkage water ratio of not more than 1:1; a modulus of rupture, when mixed with equal weights of sand, of not less than 250 pounds per square inch; a vitrification temperature of approximately 1,275°, C; an overfiring temperature not below 1,425°, C; and a softening point equivalent to Orton cone 29, or above.

The value of graphite for crucible making is expressed by the factors of density, surface factor, and ash content. Artificial graphite and coke might possibly be used, but are subject to certain limitations.

The usefulness of the Grossalmerode clay for glasshouse refractories is due principally to its low fire shrinkage. Its ability to dry without checking or cracking even under adverse conditions is another desirable feature. While its resistance to corrosion by the melt is sufficient for glasses of the soda-lime type, it does not stand up well in contact with flint glass. The rigidity of this siliceous clay at furnace temperatures—that is, its ability to resist pressure without deformation—is another point in its favor. On the other hand, it is apt to be somewhat tender as

regards mechanical manipulation in the furnace and shows a tendency to spall under sudden temperature changes.

Conversely, most American bond clays dry somewhat more difficultly than the German clay and show a greater drying and firing shrinkage. When properly prefired, on the other hand, they resist the corrosion of glass more satisfactorily. Siliceous clays are found in the United States which duplicate the Grossalmerode clay. It is not desirable to go as high as the silica content of the imported material in order that the density of structure may be not impaired too greatly. The disadvantage of the greater fire shrinkage in the furnace may be overcome, first, by the addition of a very siliceous clay in the raw state to the more aluminous bond clays; second, by the introduction of some calcined siliceous clay (grog), passing an 18-mesh sieve, in the pot batch; and, third, by prefiring the pots or blocks to a higher temperature than is customary, thus bringing about the bulk of the shrinkage before the objects are placed in the melting furnace. Large deposits of highly siliceous clays are available in the United States.

It is urged that the construction of pot arches be changed to a type making possible more uniform temperature distribution, as well as higher temperatures. The down or up draft kilns with perforated bottoms, used extensively in the clay industries, are recommended. The rate of heating the pot arches should conform to the critical temperature ranges applying to clay, viz, the expulsion of the hygroscopic and of the combined water and the oxidation of carbon. Halts should be made within these ranges until the changes involved are completed. Between and beyond the critical temperatures the heating may be more rapid than prescribed by the present practice.

For the melting of optical glass the use of semiporcelain or porcelain pots is recommended. Compositions are given for mixtures of this type. The use of waste white-ware pottery bisque is suggested as a source of grog. Finally, the procedure of casting glass pots as practiced at the Pittsburgh laboratory of the Bureau of Standards is described.

The writer desires to express his appreciation of the laborious work done by G. A. Loomis in the careful testing of the clays which have been described, and the cooperation of F. H. Riddle, J. W. Wright, and W. W. McDanel.

WASHINGTON, June 2, 1919.

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No. 145

## DIRECT DETERMINATION OF INDIA RUBBER BY THE NITROSITE METHOD

BY

JOHN B. TUTTLE, Associate Chemist

and

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*Bureau of Standards*

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# DIRECT DETERMINATION OF INDIA RUBBER BY THE NITROSITE METHOD

By John B. Tuttle[1] and Louis Yurow

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Review of previous work on nitrosite method | 4 |
| III. Analytical procedure | 5 |
| IV. Preliminary work | 5 |
| 1. Combustion apparatus | 6 |
| 2. Nitration apparatus | 7 |
| 3. Method of procedure | 7 |
| 4. Removal of acetone | 8 |
| 5. Drying | 10 |
| V. Details of the method as applied to various vulcanized rubber compounds | 10 |
| 1. Compounds containing reclaimed rubber | 11 |
| 2. Compounds containing lampblack | 11 |
| 3. Compounds containing bituminous substances | 11 |
| 4. Compounds containing oil substitutes | 12 |
| VI. Discussion of results | 12 |
| VII. Method finally adopted | 14 |
| VIII. Summary | 16 |


## I. INTRODUCTION

One of the most important determinations in the analysis of a rubber compound is that of the amount of rubber present. The two types of methods used for this purpose are the direct and indirect.

The indirect methods comprise those in which the rubber is removed from the mineral fillers, either by ignition or solution. In such methods, it is usual to determine all the other constituents of the compound, and to call the remainder "rubber by difference." One method, which is very near the border line between these types, eliminates all volatile constituents except the rubber, and determines the latter by loss on ignition. In this instance, certain corrections are necessary to secure accurate results. While some of the indirect methods have considerable value, all of them are open to more or less objection.

[1] Formerly associate chemist, Bureau of Standards, where all of the work described in this paper was done

The direct methods include those in which definite compounds of rubber are formed. These are either weighed directly, or some important constituent is determined, and the rubber calculated by means of the proper factor. It is with a modification of one of these direct methods, viz, the nitrosite method, that this paper deals.

## II. REVIEW OF PREVIOUS WORK ON NITROSITE METHOD

The original nitrosite method consists essentially in weighing the compound formed by treating rubber with the oxides of nitrogen which are evolved when nitric acid reacts with arsenic trioxide, starch, or some other reducing agents. The method was first proposed by Harries,[2] who has since published a number of articles on the subject. While other investigators have also done considerable work [3] it is not our purpose to discuss the various modifications proposed, other than to say it is generally accepted that the difficulty in securing a compound of definite composition renders the method of questionable value.

The work of Harries and others showed that there is no loss of carbon during the formation of the nitrosite. This led L. G. Wesson to the idea of burning the nitrosite, collecting the resulting carbon dioxide, and calculating from this the amount of rubber $(C_{10}H_{16})x$. The method as worked out by Wesson [4] was not entirely satisfactory because it could be used solely on soft vulcanized compounds containing only new rubber of good quality, and even then at times the results were very disappointing. All attempts to apply the method to compounds containing reclaimed rubber or substitutes failed. In view of the growing importance of the determination of rubber, and the difficulty in obtaining satisfactory results by means of the indirect methods, the authors of this paper took up the subject in order to ascertain whether or not a suitable method could be developed. A preliminary note of the work was presented orally to the rubber section of the American Chemical Society at its meeting in New York in September, 1916. At the same meeting Wesson presented a modification of his first method.[5] He believed that the difficulties with it could be eliminated by means of the wet combustion. In this modification, he worked with compounds con-

[2] Ber., **34** (1901), p. 2991; **35** (1902), p. 4429; **36** (1903), p. 1937; Z. Angew. Chem., **20** (1907), p. 1355 (1969).

[3] Alexander, Ber., **38** (1905), p. 181; **40** (1907), p. 1072; Z. Angew. Chem., **20** (1907), p. 1358; **24** (1911), p. 680; Gottlob, Z. Angew. Chem., **20** (1907), p. 2213. K. Fendler, Gummi Ztg., **24** (1910), p. 1000.

[4] L. G. Wesson, Bureau of Standards Technologic Paper No. 35; J. Ind. Eng. Chem., **6**, p. 459; 1914.

[5] Wesson and Knorr, J. Ind. Eng. Chem., **9**, p. 139; 1917.

taining only new rubber, mineral fillers, and sulphur, and while the results obtained were satisfactory, the method was still not of general application. The new method has been developed to the point where it is possible to secure excellent results on practically all classes of compounds.

## III. ANALYTICAL PROCEDURE

Wesson's original article gives very full details of the method which he employed, and inasmuch as in our preliminary work we largely followed his method, it will be worth while to give a brief outline of it. The rubber is ground to pass a 20-mesh sieve. A sample of 0.25 to 0.50 g is taken for each determination, subjected to extraction with acetone, and after removal of most of the acetone, the sample is transferred to a 50 $cm^3$ graduated flask, and allowed to swell in chloroform. The nitrosite is now formed by passing through the chloroform solution a stream of oxides of nitrogen generated by heating arsenic trioxide and nitric acid. After standing overnight, the chloroform is decanted through a Gooch crucible and the residue is washed by decantation with chloroform. After driving off the last traces of the solvent by means of a gentle current of air, the nitrosite in the crucible is dissolved in acetone and the solution is returned to the original flask and made up to the mark. The flask is stoppered and shaken, or centrifuged, to throw down the mineral matter. A 25 $cm^3$ portion of the liquid is pipetted into another flask, most of the acetone removed by evaporation, and the nitrosite transferred to the combustion boat, the final rinsing being done with ethyl acetate. The nitrosite is dried in an air bath at 85° C for two hours, burned in the combustion furnace, and the carbon dioxide collected and weighed, and from it the rubber content is calculated.

It will be seen that this gives only the percentage of rubber which is originally insoluble in acetone. In order to obtain the total amount of rubber, it will be necessary to add to the rubber thus determined, the rubber resins found in the acetone extract. The sum should correspond to the percentage of rubber added to the compound.

## IV. PRELIMINARY WORK

Our procedure in developing a satisfactory method was to check up each step of the one proposed by Wesson, in order to find out where errors occurred, and then to work out a satisfactory scheme for eliminating these errors.

### 1. COMBUSTION APPARATUS

During the combustion, the following products may be obtained which would require elimination or selective absorption in the absorption train: (1) Foreign matter in the oxygen, such as organic matter, moisture, etc.; (2) water; (3) oxides of nitrogen; (4) carbon dioxide from the nitrosite. The effects of these on the final results of our tests were ascertained by means of suitable blanks.

1. A blank determination on the oxygen was made under conditions identical with those of an actual determination. The train, arranged as used by Wesson, was as follows: Tower containing moist soda lime, bubble counter containing concentrated sulphuric acid, combustion tube, two U tubes containing glass beads and a solution of potassium bichromate in concentrated sulphuric acid, U tube with 30-mesh zinc, a special absorption tube containing soda lime followed by calcium chloride, a special absorption tube containing soda lime followed by alumina,[6] a U tube containing palladium-chloride solution. Wesson used alumina as the final drying agent, because of the claim that it is as efficient as sulphuric acid. It may be possible to prepare alumina having the same drying properties as sulphuric acid, but as a matter of general practice, the same material shouid be used before and after the soda-lime tubes.

Our first blanks showed a loss in weight of the soda-lime tubes, apparently because the alumina was less efficient than the concentrated sulphuric acid. We decided to avoid any uncertainty on this point by replacing the alumina with calcium chloride, and adding two new tubes containing bichromate and concentrated sulphuric acid, one just before the tube containing the zinc, and the other after the second soda-lime tube.[7] The latter was weighed after each determination. These tubes were filled at the same time with the same solution, so that we could be reasonably certain that the oxygen passing through the final tube which was weighed would have the same moisture content as it had when it entered the first. A new blank on the oxygen gave negative results.

2. To learn whether or not any water would be carried over into the soda-lime tubes, a small quantity of $BaCl_2.2H_2O$, containing about the quantity of water that would be formed during the combustion of the nitrosite, was heated in the boat in the usual manner.

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[6] Johnson, J., Am. Chem. Soc., 34, p. 911; 1912.

[7] The order of tubes adopted by Wesson is illustrated on p. 8 in the Bureau of Standards Technical Paper No. 35, while the authors' arrangement will be described in detail later on in this paper.

There was no appreciable change in weight, showing that no water vapor was carried over.

3. Copper nitrate was heated in the apparatus, to determine the effect of the oxides of nitrogen. No appreciable change in weight could be noted.

4. The ability of the apparatus to yield correct results for carbon dioxide was tested by burning pure sugar. The results of this experiment were satisfactory, and showed that the combustion furnace as arranged was adequate for the purpose.

### 2. NITRATION APPARATUS

When blanks on the nitration apparatus were made by conducting the nitrogen oxides through chloroform, a slight turbidity was noticed. The chloroform was evaporated off, and the residue soluble in acetone was transferred to a boat and burned in the usual manner. The amount of carbon dioxide thus obtained was considerable, amounting to 0.6 per cent or more, calculated as rubber. It was noticed that the rubber connections showed signs of having been attacked, and it was thought that small particles of rubber had been carried over mechanically. The rubber connections were then eliminated by sealing together the glass tubing. The one place where it was necessary to break the connection after each treatment was provided with a mercury seal. New blanks showed only 0.2 per cent. It is possible that by suitable purification of the chloroform, even this small amount could be eliminated. The chloroform which we used was of chemically pure quality, and was free from nonvolatile residue.

### 3. THE METHOD OF PROCEDURE

The nitrosite method is based upon the assumption that the carbon of the pure rubber substance is carried intact through the various steps in the determination, and is finally collected and weighed as carbon dioxide, and that carbon in other form which may be present in the rubber compound is eliminated at one step or another. During the nitration, mineral carbonates are decomposed with the elimination of their carbon dioxide. No organic fillers are known which upon nitration yield compounds insoluble in chloroform and soluble in acetone. If such were found, it would be, of course, necessary to devise some means of getting rid of them before proceeding with the determination of the rubber. We therefore worked upon the assumption that if we used pure gum rubber bands, no carbon other than that from the pure rubber substance would affect the result.

### 4. REMOVAL OF ACETONE

The first point investigated was the loss during the decantation of the chloroform from the nitrosite. The chloroform was evaporated off, and the residue transferred to a boat and burned as usual. The carbon dioxide thus found was equal to that obtained from 4 to 8 per cent of rubber. In an effort to eliminate this error, acetone was substituted for the chloroform in the nitration. Considerable heat was evolved, which showed that some new reaction took place. It was then found that when oxides of nitrogen were passed into redistilled acetone a considerable amount of an oily product was formed. No attempts were made to identify these products of the reaction. Check determinations were now made in which in one case, the acetone was completely removed by drying in hydrogen at 85 to 90° C, and in the other the sample was treated as directed by Wesson. The results were significant. In the chloroform solution, the acetone-free sample showed a residue of only 0.7 per cent, calculated as rubber, while the samples containing acetone showed over 9 per cent. Thus while the organic matter in the chloroform filtrate may largely result from the reaction between the oxides of nitrogen and acetone left in the rubber, there is no doubt that there is still an appreciable amount which can not be accounted for in this way. Under the circumstances, it is only reasonable to conclude that this organic matter was originally present in the rubber itself. The nature of this latter material which is carried over in the chloroform is, of course, not known, and we have had no opportunity to investigate it. The results given by Wesson in his original paper showed that a sample after standing for some weeks gave results from 1 to 2 per cent lower than those obtained when the sample was fresh. The change in the sample was probably due to oxidation, and it may be that the oxidized material does not follow the same course as the unchanged rubber. If so, this would explain why a small amount remains in the chloroform, since it is well known that even fresh rubber contains a small percentage of oxidized rubber.

It is apparent that the organic matter remaining in the chloroform from the samples which have been freed from acetone is part of the rubber. We therefore recover this portion of the rubber and include it with the nitrosite insoluble in chloroform. After filtering off the nitrosite, the filtrate is evaporated to dryness and that portion of the residue which is soluble in acetone is added to the solution in acetone of the main portion of the nitrosite.

Wesson transferred his acetone solution of the nitrosite to a 50 $cm^3$ flask from which he eventually took 25 $cm^3$ for analysis. Thus each nitration yielded only one determination. We have replaced the graduated flask with a weight burette of a special form. (See Fig. 1.) The small cup in the bottom collects the mineral sediment, allowing the clear liquid to be drawn off through

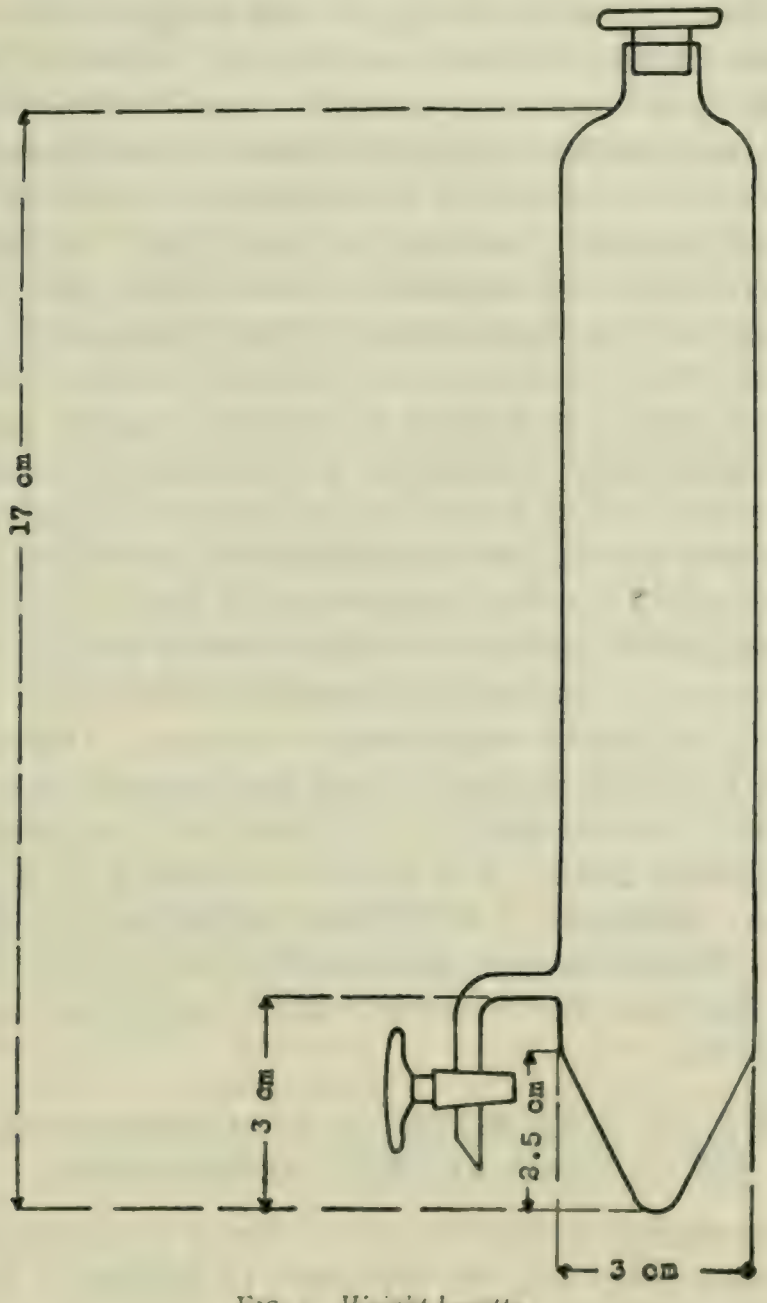


FIG. 1. *Weight burette*

the stopcock. The burette is, of course, weighed before and after drawing off the liquid. The weight of the burette empty is known, and consequently the total amount of liquid and the portion drawn off for analysis can easily be calculated. There is an advantage in using the weight burette in that other portions can be drawn off for check determinations.

### 5. DRYING

There was one more point where an error of considerable size could be introduced unless uniform conditions were maintained. This was in the drying of the nitrosite previous to combustion. Wesson recommended drying at 85° C for 2 hours. A number of determinations were made in which the further loss in weight after the first 2 hours' drying at this temperature was noted. These results varied from 0.007 to 0.017 g. About 15 hours were required to obtain constant weight. Some of this loss in weight may have been moisture originally present in the organic solvents, and, of course, this moisture would have no effect on the determination of carbon. However, at least part of this loss undoubtedly represented organic solvents held by the gummy nitrosite, and to this extent an error was introduced. It is quite possible, therefore, that some of Wesson's results which agreed very closely with the amount of rubber actually put into the compound were really obtained by a fortunate balancing of errors.

It is evident that 15 hours' drying is out of the question. In Wesson's work on the wet combustion he attempted to remedy this defect, which we had pointed out to him in a private communication. After drying for a short time to remove the greater part of the acetone and ethyl acetate, he added water and hydrochloric acid, and again evaporated to dryness. The objection to the use of hydrochloric acid is that the nitrosite is insoluble in acid solution; consequently it is difficult for the water to penetrate the gummy mass. The nitrosite is soluble in alkalies, and we therefore moistened it with water made faintly alkaline with ammonia. The results were exceedingly satisfactory; in this way we found we were able to remove all of the organic solvent in a very short time.

## V. DETAILS OF THE METHOD AS APPLIED TO VARIOUS VULCANIZED RUBBER COMPOUNDS

By the preliminary work described above a method was developed by means of which we were able to determine with a considerable degree of accuracy the percentage of rubber present in compounds containing only new rubber, sulphur, and inorganic mineral fillers. Our efforts were then directed toward extending the use of the method to such compounds as contained reclaimed rubber, lampblack, bituminous substances or the so-called "mineral rubbers," oil substitutes, etc.

### 1. COMPOUNDS CONTAINING RECLAIMED RUBBER

No changes were found to be necessary in order to apply the method to compounds containing reclaimed rubber. In such cases, of course, the acetone extract is much higher than usual, owing to the presence of mineral oils in the reclaimed rubber, and it would not be just to add the total amount of the acetone extract to the rubber hydrocarbons determined, in order to ascertain the actual amount of rubber added. An arbitrary correction must be made, and it probably will be sufficiently accurate if it is assumed that the acetone extract of the rubber itself is 4 per cent, as indicated by the experience of this Bureau. The rubber hydrocarbons determined are, therefore, 96 per cent of the total rubber present, and the proper calculations should be made. The corrected figure thus obtained will probably be more accurate than that obtained by any other method in use to-day.

### 2. COMPOUNDS CONTAINING LAMPBLACK

Lampblack offered no special difficulties in the way of determining the amount of rubber present. It was not acted upon during nitration, and while some of it was carried over with the nitrosite into the acetone solution, it was completely separated from the latter when it collected in the cup in the bottom of the weight burette.

### 3. COMPOUNDS CONTAINING BITUMINOUS SUBSTANCES

A slight modification of the ordinary method was found necessary whenever bituminous substances were present. The sample was extracted with acetone as usual. If after drying, upon placing the sample in the chloroform, a dark-colored solution resulted, the solution was filtered through a paper extraction thimble, the sample and filtrate were placed in the extraction apparatus, and the sample was extracted with chloroform for four hours. After extraction the rubber was transferred to the nitration apparatus, fresh chloroform added, and the nitration carried on as usual. The rest of the method was as before.

The calculation of the percentage of rubber from these tests is a more complicated problem. The acetone and chloroform extracts contain, in addition to the soluble portions of the mineral rubber, certain resins and other substances of the rubber. It is therefore necessary to assume an arbitrary correction, based upon the amount of material ordinarily extracted by these reagents from new rubber. We have already stated that we have taken 4

per cent as a fair value for acetone-soluble constituents. The chloroform extract of correctly vulcanized rubber is less than this, and we have arbitrarily chosen 2 per cent. This latter figure was derived from the results of a large number of tests made at this Bureau over a number of years. If reclaimed rubber is present this figure will be low, but even under such conditions we believe the differences will not be such as to materially lessen the value of the determination.

### 4. COMPOUNDS CONTAINING OIL SUBSTITUTES

Tests made on compounds containing oil substitutes gave very high results for rubber, showing that part at least of the oil substitutes was carried along in the same manner as the nitrosite. It is evident, therefore, that these substitutes must be removed before nitration. In the course of routine analyses, the rubber is extracted with acetone, and, in the absence of mineral rubbers, is then treated with alcoholic potassium or sodium hydroxide.[8] The same procedure was followed in this work, and after extraction with alkali the sample was dried, suspended in chloroform, and nitrated in the usual way.

## VI. DISCUSSION OF RESULTS

**TABLE 1.—Composition of Samples Tested**

| | Sample number | | | | |
|---|---|---|---|---|---|
| | E159 | BS45 | BS53 | BS65 | BS109 |
| **Rubber:** | Per cent | Per cent | Per cent | Per cent | Per cent |
| Smoked sheets | 33 | ..... | ..... | ..... | ..... |
| Pale crepe | ..... | 30 | 48 | 49.2 | 9.1 |
| Reclaimed | ..... | ..... | ..... | ..... | [a] 79.8 |
| **Substitutes:** | | | | | |
| Black corn No. 2 | ..... | 15 | ..... | ..... | ..... |
| M. R. X | ..... | ..... | ..... | 24.6 | ..... |
| **Fillers:** | | | | | |
| Lampblack | ..... | ..... | 4 | ..... | ..... |
| Whiting | 29 | 25 | ..... | ..... | ..... |
| Zinc oxide | 30 | 20 | 22 | ..... | ..... |
| Litharge | 5 | 7 | 24 | 24.6 | 6.4 |
| Sulphur | 2 | 3 | 2 | 1.6 | 4.7 |
| Paraffin | 1 | ..... | ..... | ..... | ..... |

[a] This reclaimed rubber, on analysis, gave 61.3 per cent rubber and organic extract. The percentage of 79.8 reclaimed corresponds to 48.9 per cent in the rubber from this source, which with the 9.1 per cent of new rubber gives a total rubber content of 58 per cent.

In Table 1, we give the composition of the samples used specially in this work. Sample E159 was prepared by a rubber company for another investigation, and the formula given is that furnished

[8] See Bureau of Standards Circular No. 38, p. 71.

by it. From the results obtained in this other investigation, we believe the composition as given to be accurate. The other samples were mixed and vulcanized at this Bureau. Table 2 gives the results obtained on these samples when using our method.

**TABLE 2.—Results of Analyses**

| Sample No. | Rubber calculated per cent | Rubber found | | | | |
|---|---|---|---|---|---|---|
| | | Per cent | Per cent | Per cent | Per cent | Per cent |
| E159 [a] | 33.0 | 34.2 | 32.6 | 33.5 | 34.8 | 33.1 |
| BS45 | 30.0 | 29.8 | 30.0 | 30.6 | 30.6 | ..... |
| BS53 | 48.0 | 48.7 | 48.6 | 48.1 | ..... | ..... |
| BS65 | 49.2 | 49.4 | 49.2 | 48.9 | 48.9 | ..... |
| BS109 | 58.0 | Series a | | 56.6 | 57.2 | 58.8 |
| | | Series b | | 59.3 | 59.4 | 60.8 |
| | | Series c | | 55.9 | 56.6 | 56.7 |
| | | Series d | | 58.1 | 59.5 | 60.2 |
| | | Average of 12 determinations | | | | 58.3 |

[a] The results on E159 were obtained before adopting ammonia in the drying of the nitrosite before combustion. The somewhat higher results in two of the determinations are undoubtedly caused by the occlusion of small quantities of organic solvents.

From the foregoing it is apparent that with compounds containing only new rubber, a high degree of accuracy is attainable. Lampblack does not interfere with the analysis. When reclaimed rubber is present, there is apt to be a greater variation in the results than when only new rubber is present. This is not surprising, for it must be realized that with material of this nature there is bound to be considerable variation in composition in the material itself, and we must expect the results to vary more than usual. With further experience it may be found that slight changes in the manipulation will bring about increased accuracy, but even now we believe that the results are sufficiently accurate for all practical purposes.

It should be remembered that this method does not attempt to discriminate between new and reclaimed rubber; as far as we know there is no quantitative method to-day which will determine the percentage of either kind in a mixture of the two. Our method gives merely the total of the two kinds, and the average quality must be determined by means of the usual mechanical tests of tensile strength, elongation, permanent set, etc.

When oil substitutes are present, the results are again not as good as when only new rubber is used, but on the whole are satisfactory and usually more accurate than when reclaimed rubber is present.

We have as yet found no fillers, organic or inorganic, which interfere with the accuracy of the method. Mineral carbonates are decomposed in the acid solution and the carbon dioxide is driven off during evaporation. As will be seen from Table 1, we tested compounds containing from 25 to 28 per cent of whiting without having it affect the results in the least. Other carbonates would act in the same way. We have had occasional tests when filter paper was allowed to remain with the rubber during the nitration. It was eliminated during the filtration of the nitrosite from the chloroform solution, since it is insoluble in acetone, and the nitrosite is soluble. The only fillers which could possibly affect the analysis are those which are insoluble in acetone, chloroform, and alcoholic potassium hydroxide, and which upon nitration produce new compounds which are soluble in acetone. With a few preliminary tests, which are usually made, it is a very simple matter to change the procedure so as to eliminate mineral rubbers and oil substitutes before they can do any harm.

During the early part of this investigation we used the furnace described by Wesson. Later, we were unable to obtain a further supply of combustion tubing. We therefore had recourse to fused silica tubes, but these presented new problems which had to be solved. It was no longer possible to fuse platinum wires in the wall of the tube, or even to draw out the latter as Wesson had done. We therefore cemented a reducing tube of Pyrex glass to the silica tube, using de Khotinsky cement. The Pyrex reducing tube at one end was just large enough to slip over the silica tube, and the other end was drawn down to the same size as that of the glass tubing on the first absorption bottle. For a catalyzer we used platinized asbestos, heated with a gas flame. The radiation from this heating occasionally softened the de Khotinsky cement and we arranged a cooling device by wrapping the silica-Pyrex joint with a strip of cotton cloth about 4 cm wide, the loose end of which dipped down into a beaker of water. The cotton strip was thus kept moist and effectually kept the temperature of the cement at a safe point.

## VII. METHOD FINALLY ADOPTED

Preliminary extractions of a 2 g sample are made according to the usual methods of the Bureau of Standards[9] to determine the amount of acetone, chloroform, and alcoholic potash extracts.

[9] Bureau of Standards Circular No. 38.

These extractions will prove the presence or absence of mineral rubbers and oil substitutes. In the absence of both, proceed as below. If mineral rubbers are present, make a chloroform extraction; if oil substitutes, an alcoholic potash extraction; and if both are present make both extractions. In every case make these extractions after the acetone extraction, and before the sample is allowed to swell in chloroform.

Take 0.500 to 1.000 g of the finely-ground sample (call this weight *W*), extract with acetone for 8 hours, and if necessary with chloroform and alcoholic potash. Dry the residue in hydrogen (or other inert gas) for 2 hours at 100° C. Place the sample in 50 to 75 $cm^3$ of chloroform, and allow it to swell. Immerse the flask containing the rubber in cold water and pass into this, until the green color which is formed persists for 30 minutes, the gases formed by heating arsenic trioxide and nitric acid of specific gravity 1.30. It is important here, in order to avoid contamination, that no rubber connections be used. Allow the solution to stand overnight; the next day, filter off the nitrosite through a Gooch crucible and wash with small quantities of chloroform. Remove the acid gases and chloroform from the flask by means of a gentle current of air. Evaporate the filtrate to dryness. Dissolve in acetone the nitrosite remaining in the flask, on the Gooch crucible, and in the residue from the filtrate, and filter the solution through asbestos into the weight burette. The total volume should be about 100 $cm^3$. Allow this solution to stand a short time so as to permit any sediment which may form to settle out in the bottom of the weight burette. Weigh the burette before and after filling, calling the difference *N*. Draw off about 25 $cm^3$ into a small Erlenmeyer flask, reweigh the burette and call the difference *O*. Evaporate the portion drawn off to a small volume, transfer to a porcelain boat (about 14 cm long, and 1 cm wide) which has been filled with alundum, and wash the flask with acetone. It is best to make this transfer in small portions, drying the boat and contents for a few minutes between each addition. After the final washing and drying, add 1 or 2 $cm^3$ of a 1 per cent solution of ammonia in distilled water and dry in an inert gas for 1 hour at 90° C. Repeat with a second portion of ammonia and dry as before. By this means, all of the organic solvent will be removed.

Place the boat in the furnace and proceed with the combustion as usual. The furnace, of whatever type used, should be carefully tested before using. Pass the products of combustion through

U tubes or other satisfactory absorption tubes, placed in the following order; *a*, *b*, *c*, potassium bichromate-concentrated sulphuric acid; *d*, powdered zinc, 20-mesh; *e*, *f*, soda lime and calcium chloride; *g*, potassium bichromate-concentrated sulphuric acid; *h*, dilute palladium chloride solution. Very little palladium chloride is needed. We use about one drop of 10 per cent solution in 10 $cm^3$ of distilled water. Weigh *e*, *f*, and *g* before and after each combustion; refill *c* and *g* frequently from the same solution so that the gases which enter *e* and those that leave *g* will have the same moisture content. The palladium chloride serves to detect the presence of carbon monoxide; if there is any blackening, it shows incomplete oxidation. In this event, discard the results and repeat the determination.

The carbon dioxide will equal the algebraic sum of the differences in tubes *e*, *f*, and *g*. Call this *P*. The factor for calculating from carbon dioxide to rubber hydrocarbons is 0.309. The formula is therefore as follows:

$P \times 0.309 \times \frac{N}{O} \times \frac{100}{W}$ = Percentage of rubber hydrocarbons. Correct this figure for whatever extractions were made previous to nitration.

## VIII. SUMMARY

Harries and his coworkers claimed that there is no loss of carbon when the rubber molecule passes through the process for the formation of the nitrosite. Wesson's combustion method for the direct determination of rubber depends upon the correctness of this claim. An examination of his method shows that, although he obtained fairly satisfactory results, there are certain avoidable sources of error. Compounds containing new rubber and no substitutes or organic fillers, can be analyzed with correct results, owing to a balancing of errors.

By suitable changes in the procedure of Wesson the present authors have succeeded in obtaining very satisfactory results, not only with pure gum compounds, but also with compounds made up with reclaimed rubber, mineral rubber, oil substitutes, lampblack, etc.

WASHINGTON, June 20, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 146

# CADMIUM ELECTRODE FOR STORAGE-BATTERY TESTING

BY

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*Bureau of Standards*

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By H. D. Holler and J. M. Braham

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Scope of investigation | 4 |
| III. The standard electrode | 5 |
| IV. Reproducibility of cadmium electrodes | 5 |
| V. Effect of temperature | 7 |
| VI. Effect of drying electrodes | 7 |
| VII. Measurement of potentials of storage battery plates | 8 |
| VIII. Polarization of cadmium electrode | 10 |
| 1. General | 10 |
| 2. Method of measurement | 11 |
| 3. Effect of size and shape | 12 |
| 4. Effect of depth in electrolyte | 13 |
| 5. Significance of polarization error | 14 |
| IX. Conclusions | 15 |


## I. INTRODUCTION

In the operation and testing of storage cells it is frequently important, particularly in cases of low capacity, to know the individual potentials of the positive and negative plates of the cell. No standard method of measuring the potentials of storage-battery plates is recognized in the industry, but for many years the most common method has consisted simply in measuring, with an ordinary voltmeter, the potential difference between either plate of the cell and a piece of cadmium metal dipping into the electrolyte of the cell. Since the resistance of different voltmeters in common use varies over a wide range, it would not be surprising if different results were obtained with different voltmeters. Certain instances have been called to the authors' attention in which the sum of the cadmium-positive and cadmium-negative potentials is less than the cell voltage.

Since the Bureau of Standards requires for test purposes more accurate information about the reliability of this method, this investigation was undertaken to obtain experimental data which would give the information desired.

Several authors [1] have suggested the use of other electrodes for this purpose, viz, lead, lead peroxide, zinc, hydrogen, and the mercurous-sulphate electrode. The hydrogen electrode and mercurous-sulphate electrode are the most accurate and can be used in the laboratory, but are not well adapted to ordinary commercial testing. While any metal whose ions are harmless to the storage cell might be used, cadmium has been found by experience to be the most satisfactory.

## II. SCOPE OF INVESTIGATION

In order to obtain definite information in regard to the conditions under which the cadmium electrode is used in present commercial practice, and to serve as a guide for our investigation, a letter was sent to a number of representative manufacturers of storage batteries asking the following questions:

1. What precautions are necessary in its use?
2. Can it be used with an ordinary voltmeter and what should be the resistance of the voltmeter?
3. Is it generally used to measure both plates or only one? Are its indications equally reliable for either plate?
4. What are the practical objections to its use?

Many of the manufacturers kindly replied to these questions. Their replies, for the most part, indicated that no special precautions were considered necessary, and no serious objections were offered to its use, but several of them said that interpretations of the results by inexperienced observers might be misleading. All agreed that the readings on both plates are equally reliable, but in some cases they said that only the potential of the positive is to be measured, from which the cell voltage is subtracted to give the potential of the negative plate. All, with one exception, agreed that any voltmeter of proper scale is satisfactory, the resistance of the instrument being considered of no importance.

It was necessary first to obtain an electrode as a standard with which a comparison of the cadmium electrodes could be made. The mercurous-sulphate half cell was adopted for this purpose. The reproducibility of the cadmium electrode was first determined and then the effect of temperature, drying of the electrode, and polarization of the electrode were studied. The reliability of the cadmium electrode for measuring the potentials of storage-battery plates during charge and discharge was also determined. The

[1] Trout, The Electrical News, **20**, p. 42; 1911. Jumau, L'Eclairage Electrique, **24**, p. 59; 1900. Jumau, Les Accumulateurs Electriques, p. 109; 1904. Liagre, L'Eclairage Electrique, **40**, p. 406; 1904.

most important part of the investigation proved to be the effect of polarization of the cadmium electrode upon the measurement of the potential of the positive plate.

The present investigation deals only with the accuracy of the cadmium electrode and does not discuss the cadmium readings with reference to the age or condition of the battery.

## III. THE STANDARD ELECTRODE

As a standard electrode with which comparison of the cadmium electrode could be made a mercurous sulphate-sulphuric acid electrode of the form suggested by G. N. Lewis[2] was employed. The advantages of this electrode, aside from its high degree of reproducibility and constancy, is its common-ion constituency and the harmlessness of its components if introduced into the storage cell. For the precise measurement of potentials of storage-battery plates, the mercurous-sulphate electrode with a potentiometer is highly satisfactory and recommended for laboratory work, but not in commercial practice by ordinary operators.[3]

In order to minimize the liquid contact potential difference between the electrolyte of the storage cell and that of the half cell, the mercurous sulphate half cell was filled with pure sulphuric acid having a density of 1.250 at 25° C. The mercurous sulphate used was taken from a lot which had been specially prepared for use in the construction of Weston standard cells. Several of these half-cells were carefully prepared and checked against each other at frequent intervals of time. Variations in their values were negligible as compared with the differences in value of different cadmium electrodes under apparently identical conditions. All the results in this paper are referred to the mercurous-sulphate electrode containing sulphuric acid of density 1.250 at 25° C.

## IV. REPRODUCIBILITY OF CADMIUM ELECTRODES

In order to determine the degree of uniformity of different cadmium electrodes, a number were prepared by sawing some of the ordinary cast metal sticks of about 0.75 cm in diameter into lengths of about 7.5 cm. These electrodes were introduced into sulphuric acid (sp. gr. 1.25) to a depth of about 2.5 cm and meas-

[2] Lewis, Jour. Am Chem Soc., **89**, p 2251; 1917.

[3] The mercurous-sulphate electrode is much more polarizable than the cadmium electrode. For instance, a resistance of 10 000 ohms in parallel with the potentiometer lowered the mercury potential 44 millivolts as compared with a lowering of the cadmium potential of only a few tenths of a millivolt.

urements with a potentiometer were made daily until consistent readings were obtained, which are given in Table 1. The electrodes, *L*, *M*, and *N* were heavily amalgamated, and *O* had been kept in acid for a month preceding this experiment.

It is to be noted that for two or three days after putting the electrodes into the acid, the potentials of different unamalgamated electrodes were different from each other by as much as 0.021 volt, for example, in the case of *D* and K, while the value of a given electrode was sometimes very erratic, for example, *K*. At the end of four or five days, after very marked corrosion was apparent, the values of different electrodes agreed within 0.01 volt.

As is evident in the case of *L*, *M*, and *N* the amalgamated electrodes exerted a potential less negative than that of pure cadmium, which is characteristic of cadmium amalgams.[4]

The variability of the values for freshly amalgamated cadmium is extreme as shown in Table 1 by the readings of *L*, *M*, and *N* on the first day. On the fourth day, however, corrosion had occurred to the extent that their values were in fair agreement. Presumably the gradually decreasing values on successive days are due to the formation of an increasing concentration of cadmium sulphate at the surface of the metal. From these observations it is evident that for satisfactory readings the cadmium electrode should be "aged" several days in battery acid until the surface of the metal is thoroughly corroded. Electrodes aged for several weeks gave the best results.

**TABLE 1.—Reproducibility of Cadmium Electrode**

[Electromotive Force (Volts) on Different Days]

| Electrode | June 14 | June 15 | June 16 | June 17 |
|---|---|---|---|---|
| A | −1.108 | −1.108 | −1.103 | −1.106 |
| B | −1.103 | −1.102 | −1.105 | −1.104 |
| C | −1.109 | −1.103 | −1.108 | −1.107 |
| D | −1 101 | −1.100 | −1.100 | −1.100 |
| E | −1.105 | −1.099 | −1.102 | −1.102 |
| F | −1.105 | −1.107 | −1.106 | −1.107 |
| G | −1.114 | −1.113 | −1.111 | −1.109 |
| H | −1.112 | −1.111 | −1.109 | −1.104 |
| I | −1.111 | [a] −1.101 | −1.106 | −1.106 |
| J | −1.110 | −1.100 | −1.108 | −1.109 |
| K | [a] −1.122 | [a] −1.093 | −1.109 | −1.108 |
| L[b] | [a] −1.053 | −1.094 | −1.093 | −1.092 |
| M[b] | [a] −1.086 | −1.100 | −1.100 | −1.098 |
| N[b] | [a] −1.084 | −1.101 | −1.099 | −1.095 |
| O[c] | −1.110 | −1.108 | −1.105 | −1.104 |

[4] Jaeger, Wied. Ann., 65, p. 106; 1898.

[a] Unsteady reading.

[b] Heavily amalgamated.

[c] Soaked in acid one month.

As indicative of the degree of constancy of a well-corroded electrode, which was initially slightly amalgamated, the following readings extending over a period of one month are given in Table 2:

TABLE 2

| Date | Electromotive force (volts) | Date | Electromotive force (volts) | Date | Electromotive force (volts) |
|---|---|---|---|---|---|
| May 17 | −1.097 | May 29 | −1.092 | June 7 | −1.100 |
| May 19 | −1.093 | May 31 | −1.095 | June 16 | −1.088 |
| May 20 | −1.091 | June 2 | −1.094 | June 18 | −1.096 |
| May 21 | −1.087 | June 3 | −1.083 | June 19 | −1.094 |

The maximum difference in the readings was 0.023, the difference between the minimum reading of —1.087 on May 21 and the maximum reading of —1.100 on June 7.

## V. EFFECT OF TEMPERATURE

To determine the effect of change in temperature upon the potential of the cadmium electrode, the vessel holding the electrodes *I*, *J*, *K*, *M*, *N*, and *O* was set into a large oil bath, the temperature of which was slowly raised from room temperature (about 25° C) to about 40° C. (This range in temperature was taken as comparable with the maximum range in temperature of a storage battery in action.) It is sufficient to state that the maximum change in the average of the potentials of *I*, *J*, and *K* was only +0.0015 volt, and the corresponding change of *L*, *M*, and *N* was −0.0036 volt for a change in temperature of 15° C. Obviously the variation of potential due to temperature is negligible as compared with variations between different electrodes.

## VI. EFFECT OF DRYING ELECTRODES

In the directions for the use of the cadmium electrode the precaution is usually emphasized that it is necessary to keep the electrode in "battery acid" so that it may be in proper condition for immediate use at any time. The importance of this point is illustrated by the following experiment, which was duplicated by several electrodes.

A well corroded cadmium electrode was removed from the acid and allowed to dry overnight. On the following morning it was returned to the acid and measurements in terms of the mercurous sulphate half-cell were immediately begun.

**TABLE 3**

| Minutes after immersion in acid | Electromotive force (volts) | Minutes after immersion in acid | Electromotive force (volts) |
|---|---|---|---|
| 0 | −1.0855 | 10 | −1.1035 |
| 2 | −1.0884 | 27 | −1.1064 |
| 7 | −1.1011 | 40 | −1.1066 |

The results in Table 3 show the necessity of soaking the electrode in acid for at least one-half hour before use, as otherwise an error of 0.02 volt may occur on this account.

## VII. MEASUREMENT OF POTENTIALS OF STORAGE BATTERY PLATES

In connection with the testing of storage batteries at this Bureau both the cadmium electrode and mercurous-sulphate electrode were used for measuring the plate potentials during charge and discharge at different rates. From a large number of curves obtained two are given in Figs. 1 and 2 as typical ones.

The curves in Fig. 1 were obtained with a single storage cell charging at a constant current of 14 amperes which was about the 5-hour rate. The cadmium electrode used was similar to those already described and had been corroded in acid for several weeks. It was contained in a perforated glass tube to avoid any possibility of its touching the plates and extended vertically through the vent of the cell into the electrolyte about 2.5 cm. Any device of insulating material not attacked by the acid is suitable for eliminating any possibility of contact with the plates. During charge the density of the acid increased from 1.160 to 1.285.

The potentials of the positive and negative plates of the cell and of cadmium were all measured against the mercurous-sulphate electrode with a potentiometer. The mercury electrode has a very convenient potential value for such measurements since it lies about midway between the positive and negative plate, so that a reversal switch permits the quick setting of the potentiometer by a small adjustment. Since each division of the ordinate in Fig. 1 represents 0.01 volt, it is seen that the variation of the cadmium potential during the whole period of time is considerably less than 0.01 volt. It was more steady than expected, as the 14-ampere rate of charge was maintained throughout and the gassing was so vigorous as to expel part of the electrolyte.

The curves in Fig. 2 were obtained with a single storage cell discharging at 5 amperes, which was about the 5-hour rate and in the same manner as those in Fig. 1. During discharge the density of the acid decreased from 1.250 to 1.145. The variation of the cadmium electrode here is slightly less than in the case of

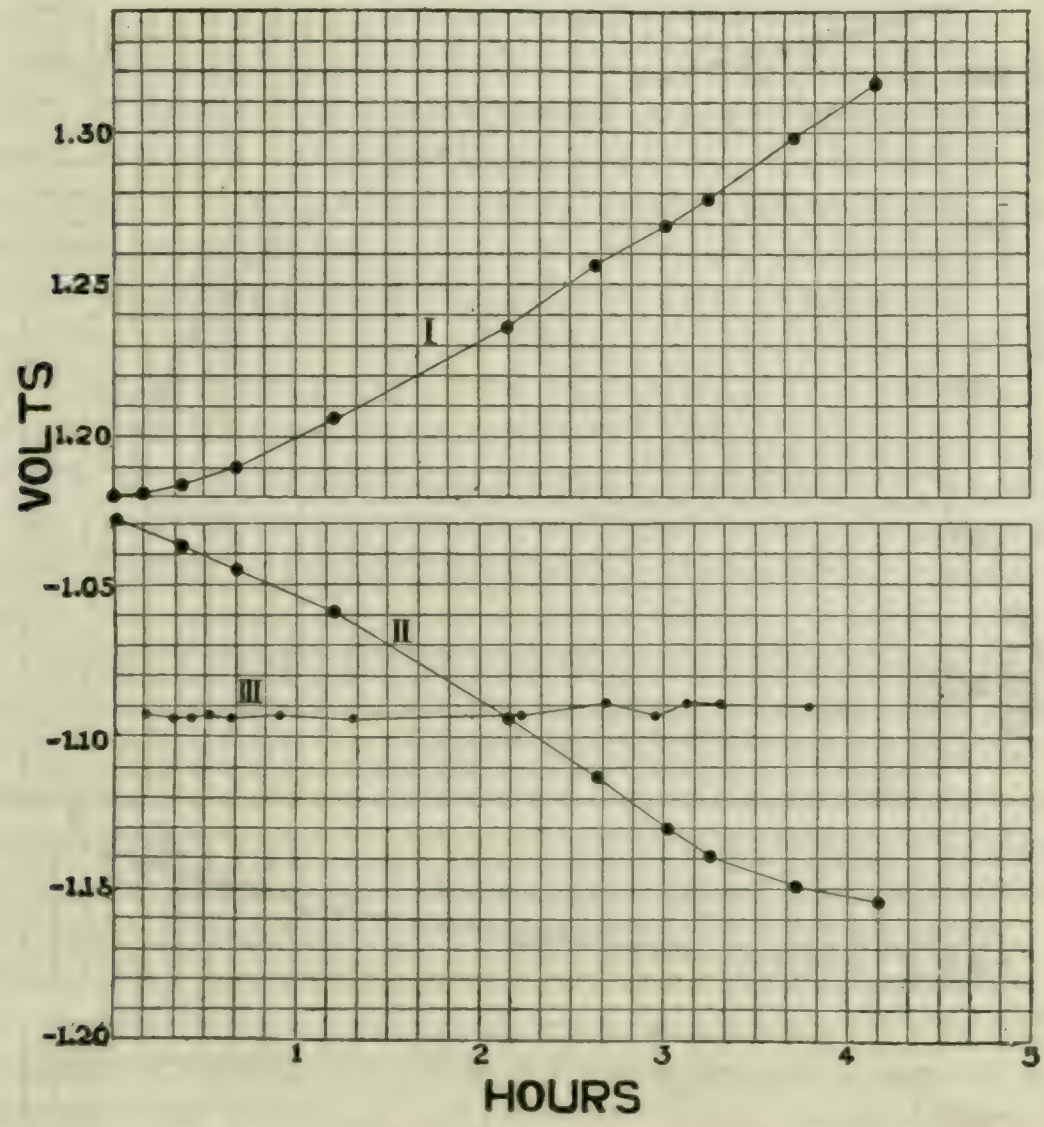


FIG. 1.—*Curve I represents the potential of the positive plate; Curve II, that of the negative plate; and Curve III that of a cadmium electrode, all measured against a mercurous sulphate electrode during the charge of the cell at a normal rate*

Fig. 1 and, in general, the readings during discharge were much more satisfactory than during charge.

It should be noted that the potential of the cadmium electrode in Fig. 1 is about 0.01 volt more negative than it is in Fig. 2. This difference represents approximately the variation to be expected of the cadmium electrode.

## VIII. POLARIZATION OF CADMIUM ELECTRODE

### 1. GENERAL

From the curves in Figs. 1 and 2 it is clear that the cadmium electrode is constant for several hours within about 0.01 volt when

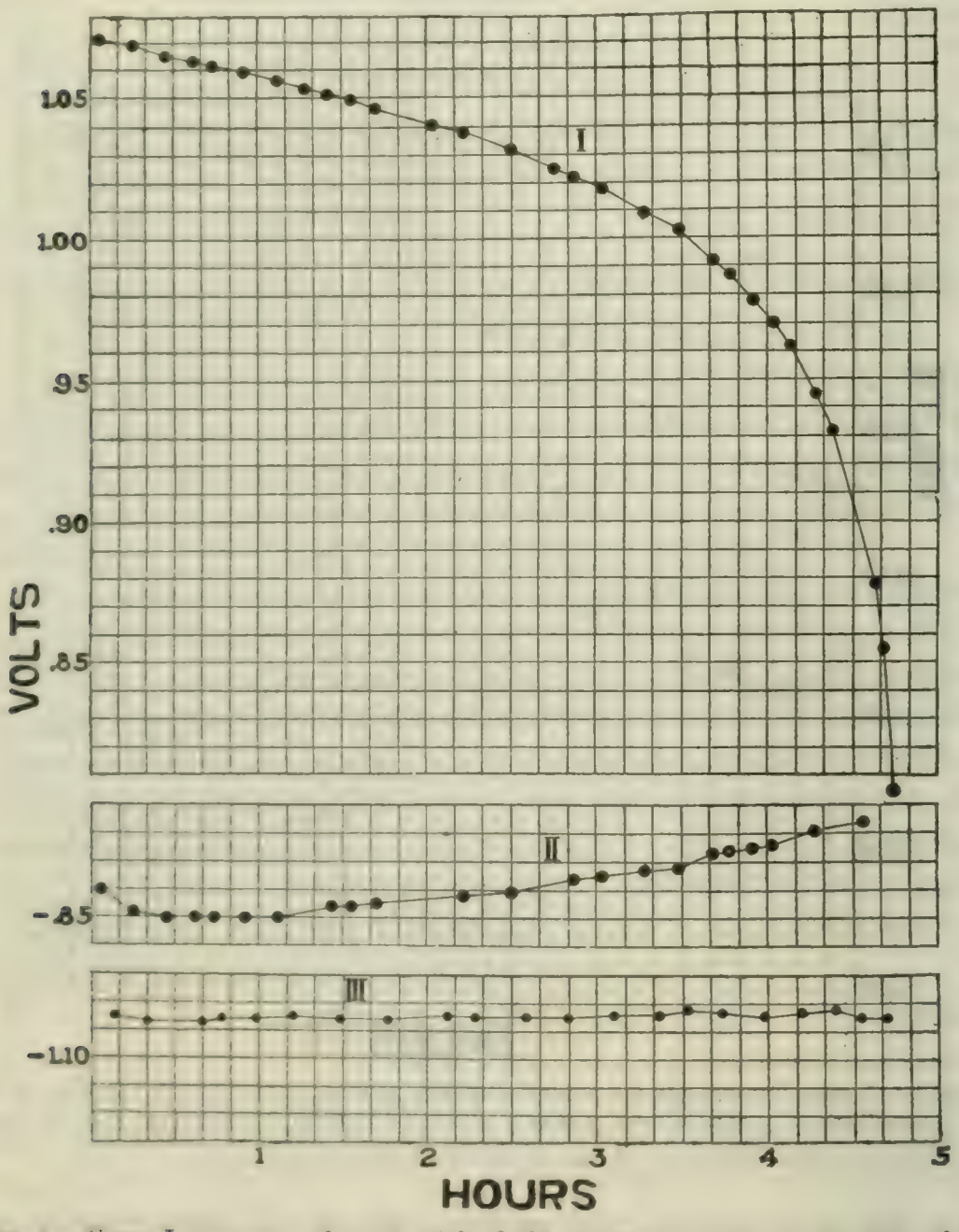


FIG. 2.—*Curve I represents the potential of the positive plate; Curve II, that of the negative plate, and Curve III, that of a cadmium electrode, all measured against a mercurous sulphate electrode during discharge of the cell at a normal rate*

the measurements are made with a potentiometer. Since, however, in commercial practice a voltmeter having a resistance of only 200 or 300 ohms is ordinarily used, it was important to determine whether the currents drawn by such an instrument

produce appreciable polarization of the cadmium electrode. For instance, in Figs. 1 or 2, if the cadmium electrode were polarized when used for making the measurements, the curve for the positive plate *I* would be too low and that for the negative plate *II* would be too high by an amount equal to the polarization of the cadmium electrode, the polarization of the plates of the cell being considered negligible.

Polarization increases with the current density on the surface of an electrode. Since the potential of the positive plate with reference to the cadmium electrode is many times that of the negative plate, the current flowing through the voltmeter when the positive plate is being measured is proportionately larger than the current flowing when the negative plate is measured. The error due to polarization in measuring the positive plate should, therefore, be much greater than for the negative plate, when a voltmeter of the same resistance is employed.

Since the current density is inversely proportional to the area of the electrode, the polarization and therefore the error in measurement should be expected to be greater the smaller the electrode used.

Although a considerable number of electrodes of different forms and sizes were tried out, the results of only a few are here given as representative of the results obtained. All electrodes were thoroughly corroded in acid before use and some were inclosed in hard-rubber cases, glass tubes, and rubber tubing, but these devices had no effect upon the readings obtained, their only advantage being protection against possible contact with the plates of the battery. Any kind of an inert insulator is equally satisfactory. The use of a porous porcelain cup was tried with the idea that the potential of the cadmium would be less affected by convection currrents. It, however, was no more nearly constant than a bare electrode

### 2. METHOD OF MEASUREMENT

The procedure employed for measuring polarization consisted simply in making a first reading of the potential of the battery plate against the cadmium electrode with a potentiometer, and then a second reading with the selected resistance in parallel with the potentiometer. The difference in the two readings is the polarization produced by the current flowing through the known resistance. The results are given in curves of Fig. 3, polarization being expressed in millivolts, for the resistances used, which were

varied from 250 to 10 000 ohms. The lower resistance (250 ohms) probably represents the resistance of the average voltmeter used in practice for such measurements. The upper resistance (10 000 ohms) represents approximately the minimum resistance which may be used without causing perceptible polarization of the cadmium electrode when measuring the positive plate.

### 3. EFFECT OF SIZE AND SHAPE

Representative types of electrodes used are given in Table 4.

TABLE 4

| Number | Type | Diameter | Depth in acid | Area of contact |
|---|---|---|---|---|
| | | Mm | Mm | $Cm^2$ |
| E1 | Rod | 7.5 | 20 | 5.2 |
| E8 | do | 4 | 25 | 3.3 |
| E5 | do | 2 | 25 | 1.6 |
| E3 | Disk | 12.5 | 25 | 6.4 |
| E6 | do | 17 | 25 | 8.8 |

Of the electrodes listed in Table 4, E1 was least polarized. The polarization of E1, when used for measuring the positive plate, is given in Fig. 3 by curve *II*, and for the negative plate by curve *IV*. Thus, with a resistance of 250 ohms, the polarization was about 33 millivolts when measuring the cadmium-positive potential of 2.176 volts, and about 2.5 millivolts when measuring the cadmium-negative potential of 0.149 volts. The ratio of the two polarization values $\frac{33}{2.5}$ $(=13)$ is approximately equal to the ratio of the two potential values $\frac{2.176}{0.149}$ $(=14)$; that is, the polarization of the cadmium electrode is directly proportional to the potential being measured.

Electrode E3 was most polarized of any electrode in Table 4. Curve *I* in Fig 3 represents the cadmium-positive potential of electrode E3 and curve *III* the cadmium-negative potential. The ratio of the polarization values in this case is $\frac{108.4}{7.6}$ $(=14.3)$.

The polarization values of the electrodes listed lie between the values for E1 and E3. Although the calculated area of E3 is slightly greater than that of E1, the polarization is greater. This is probably due to the difference in their states of corrosion which might produce a greater difference in their active surfaces than is indicated by their areas as calculated from their dimensions.

Similarly, although electrode E5 had about one-half the area of E8 their polarization values were about equal. Here also the state of corrosion was probably the determining factor.

#### 4. EFFECT OF DEPTH IN ELECTROLYTE

All measurements expressed in Fig. 3 were made upon electrodes immersed in the electrolyte 20 to 25 mm. Experiments were made

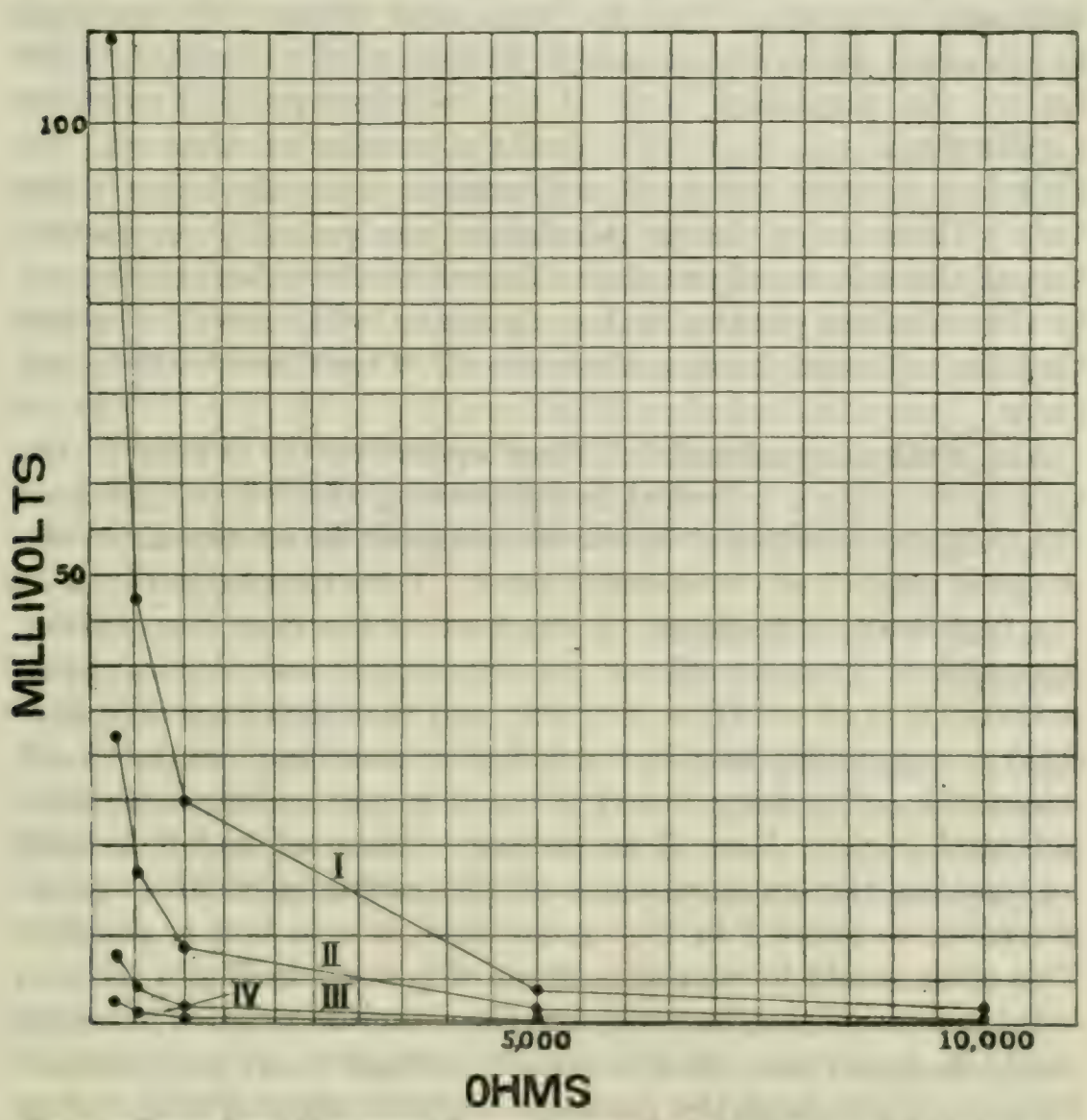


FIG. 3.—*Curves I and II represent the maximum and minimum values of the polarization of cadmium electrodes when used for measuring the potential of the positive plate with different resistances in parallel with the potentiometer. Curves III and IV represent the corresponding polarizations for the same cadmium electrodes when used for measuring the potential of the negative plate.* *For further explanation see p. 12.*

to determine the polarization of the electrodes at less depths. When the depth was decreased to 5 mm the polarization of E1 with 1000 ohms was increased from 5.4 to 8.9 millivolts. For E6 under the same conditions the polarization value changed from 4.9 to 29.5 millivolts.

The changes in polarization values of the other electrodes were between the values given for E1 and E6. It is obvious, therefore, that the electrode should extend into the electrolyte to the maximum depth possible.

### 5. SIGNIFICANCE OF POLARIZATION ERROR

The errors due to polarization are significant as shown by the following discussion. Thus, in Fig.3, when the parallel resistance is 250 ohms which is comparable with that of an ordinary voltmeter, the maximum error of the cadmium-positive potential measurement was 0.11 volt, and the maximum error of the cadmium-negative potential measurment was only about 0.008 volt. These errors due to polarization are probably representative of those in usual practice. To reduce the polarization error in the cadmium positive to less than 0.01 volt, curve *I* requires that the voltmeter have a resistance of, at least, several thousand ohms.

The method employed by some operators of obtaining the cadmium-negative potential by subtracting the cell voltage from the cadmium-positive potential as measured by an ordinary voltmeter is subject to considerable error. For example, in Fig. 2 at the beginning of discharge of the battery the cadmium-positive potential is (1.07 + 1.08) or 2.15 volts; the cadmium-negative potential is (1.08 – 0.84) or 0.24 volt; and the cell voltage is (1.07 + 0.84) or 1.91 volts; that is, the cadmium-positive potential (2.15) minus the cell voltage (1.91) is equal to the cadmium-negative potential (0.24). Now, if an ordinary voltmeter had been used for making the measurements of the cadmium-positive value, according to curve *I* in Fig. 3, an error of 0.10 volt is possible. This error would lower the position of curve *I* in Fig. 2 by 0.10 volt (10 divisions on the scale) and the cadmium-positive potential would be 2.05 volts. If now the cell voltage (1.91) is subtracted from (2.05), we have the cadmium-negative value of 0.14 volt as compared with the true value of 0.24 volt. From the curve *II* in Fig. 2 it is evident that the error of such a method of measurement is much larger than the total change in the potential during discharge.

The following procedure is suggested by which it is possible to avoid the errors described above. According to curves *III* and *IV* in Fig. 3, the error in measuring the cadmium-negative potential is very small, less than 0.01 volt, when a 250-ohm voltmeter is used. If, therefore, the cell voltage is added to the cadmium-

negative potential, the error due to polarization in measuring the cadmium-positive potential is avoided. This procedure does not permit a check upon the readings, but is free from the usual error of the cadmium-positive measurement.

## IX. CONCLUSIONS

1. The cadmium electrode is accurate to about 0.02 volt provided the proper precautions are taken. It was found to be constant within 0.01 volt during several hours, but from day to day it varied as much as 0.02 volt.

2. The cadmium electrode should be corroded several days in acid, a thorough state of corrosion being of greater importance than the exact size and shape of the electrode.

3. Amalgamation is not recommended since it makes the potential less negative and of uncertain value.

4. In case the surface of the electrode is allowed to dry, it should be soaked in acid for at least one-half hour before being used.

5. The depth of immersion should be made as great as possible, by adding electrolyte to the cell if necessary.

6. More steady readings are obtainable during discharge than during charge.

7. For accurate measurements of the potentials of storage-battery plates, the mercurous-sulphate electrode with a potentiometer is recommended.

8. The error in measurement with the cadmium electrode due to polarization is in many cases large, being proportional to the potential being measured. It is therefore many times greater in the case of the cadmium-positive than of the cadmium-negative potential.

9. The greatest error in the use of the cadmium electrode is due to polarization caused by a voltmeter of low resistence. Obviously this error may be avoided by using an instrument having a resistance of several thousand ohms. In case a voltmeter of low resistance must be used, the best procedure is to measure the cadmium-negative potential to which the cell voltage may be added to obtain the cadmium-positive potential. If a check upon the readings is required, then either a potentiometer or a high-resistance voltmeter is necessary.

WASHINGTON, August 4, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

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# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 147

# AN APPARATUS FOR MEASURING THE RELATIVE WEAR OF SOLE LEATHERS, AND THE RESULTS OBTAINED WITH LEATHER FROM DIFFERENT PARTS OF A HIDE

BY

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*Bureau of Standards*

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# AN APPARATUS FOR MEASURING THE RELATIVE WEAR OF SOLE LEATHERS, AND THE RESULTS OBTAINED WITH LEATHER FROM DIFFERENT PARTS OF A HIDE

By R. W. Hart and R. C. Bowker

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Wearing-test machines | 3 |
| III. Methods | 5 |
| IV. Results of tests | 5 |
| V. Conclusions | 10 |


## I. INTRODUCTION

The quality of sole leather is affected by many factors, such as the breed of the animal, its mode of life, the time of killing, the method of preserving the hide, and the kind of tannage. A very important factor which influences the durability of any particular sole is the part of the hide from which it is cut. It is a difficult problem to measure the wear of sole leather and generally it is accomplished by actual service tests on individuals. Such a method takes considerable time, and the value of the results obtained is often uncertain on account of the many uncontrollable variables occurring in the types of service and among the individuals wearing the soles. The development of a simple method for quickly determining the durability of sole leather seemed desirable, and this paper discusses a laboratory apparatus designed for this purpose and also presents the results of tests made to date to determine the relative wear of leather from different parts of a hide.

## II. WEARING-TEST MACHINE

A machine has been developed at the Bureau for testing the durability of sole leather with the idea of subjecting the leather to shearing action during the wear similar to that occurring in service on shoes and at the same time accelerating the actual wearing away of the material so that an indication of the durability of the specimen might be obtained in about 24 hours. The

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machine as first designed (Fig. 1) embodied a cam of clover-leaf shape, to which the samples were attached, and which rested on a horizontal disk having an abrasive surface of cement. The difficulties with this design were that the samples were submitted to a bumping action which caused the wear of each sample to be so localized that it was often worn through on one end before the other end showed appreciable wear, that no means was provided for removing the material worn away, and that the abrasive material soon wore smooth which caused a longer time to be necessary for a test. The machine (Fig. 2) as later developed and as now used is described as follows:

A wheel of 15-inch diameter carries on its face 12 test pieces. The wheel revolves at the rate of 30 revolutions per minute about a horizontal axis with its bearings in two parallel metal bars which are pivoted at one end, the other end being free. The wheel carrying the weight of the bars (and any additional weight that may be suspended from their free ends), rests on a horizontal disk of 16-inch diameter, the point of contact being 5½ inches from the axis of the disk. This disk has a surface of carborundum, and rotates about a vertical axis on which is a brake wheel provided with a brake strap, by means of which any desired resistance to rotation may be secured by the application of dead-weight. The wheel is driven by a chain and in turn drives the horizontal disk with which the test pieces are in contact. The apparatus is designed with the view of subjecting the test piece to (1) a driving (shearing) action under pressure, and (2) a slight abrasive action resulting from the circular path of contact between the wheel and disk. The conditions of pressure and shear may be adjusted as desired. A circular brush is shown resting on the carborundum disk. This brush in connection with a small exhauster tends to keep the surface of the wearing disk clean.

A test usually consists of 40 000 revolutions of the wheel which corresponds with 40 000 steps, or approximately 40 miles of walking.

The substitution of a wheel for the cam eliminated the bumping action but retained the shearing action and resulted in a more even and smoother operation. The use of a wheel allowed more specimens to be tested at one time, the entire surfaces of which were subjected to the wearing action. By using carborundum for an abrasive, a material was obtained which did not become dull or smooth quickly and which could be resurfaced with an emery-wheel dresser.

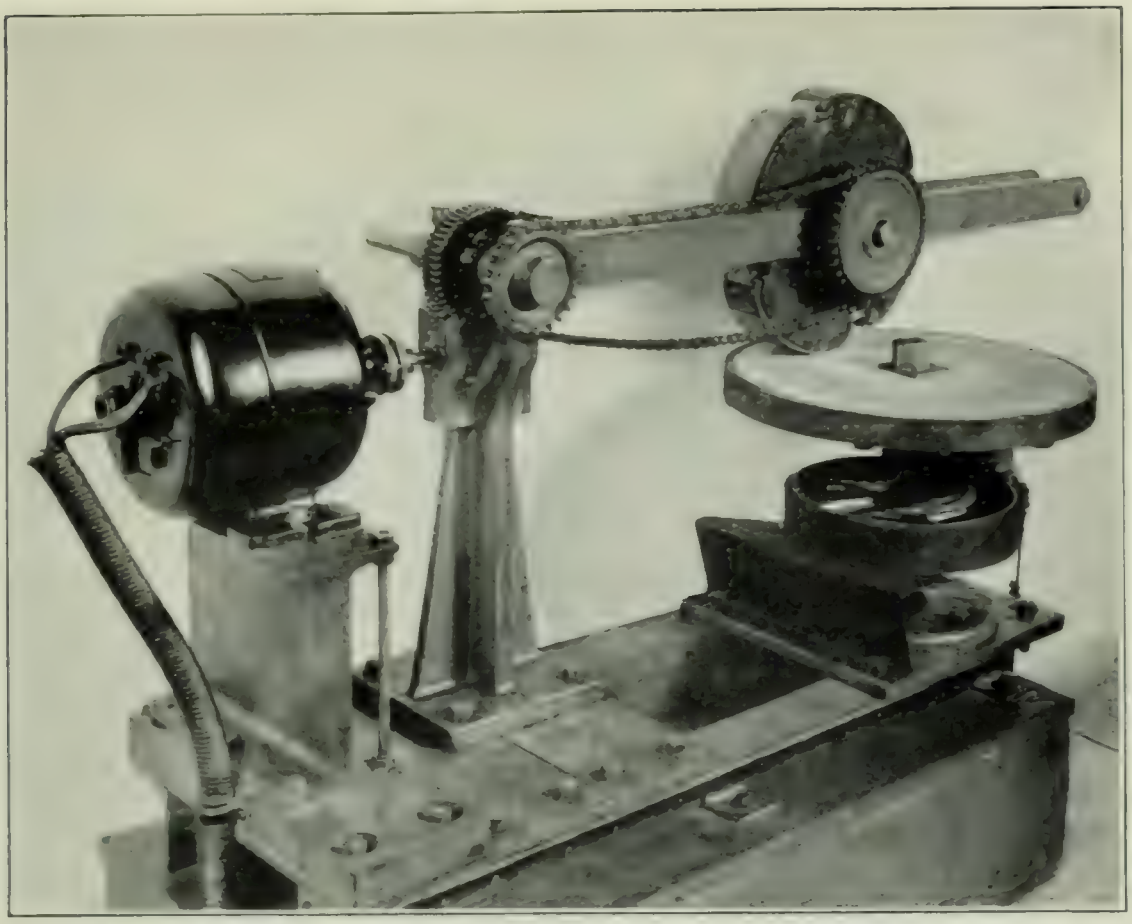

FIG. 1.—*Wearing test machine as first used*

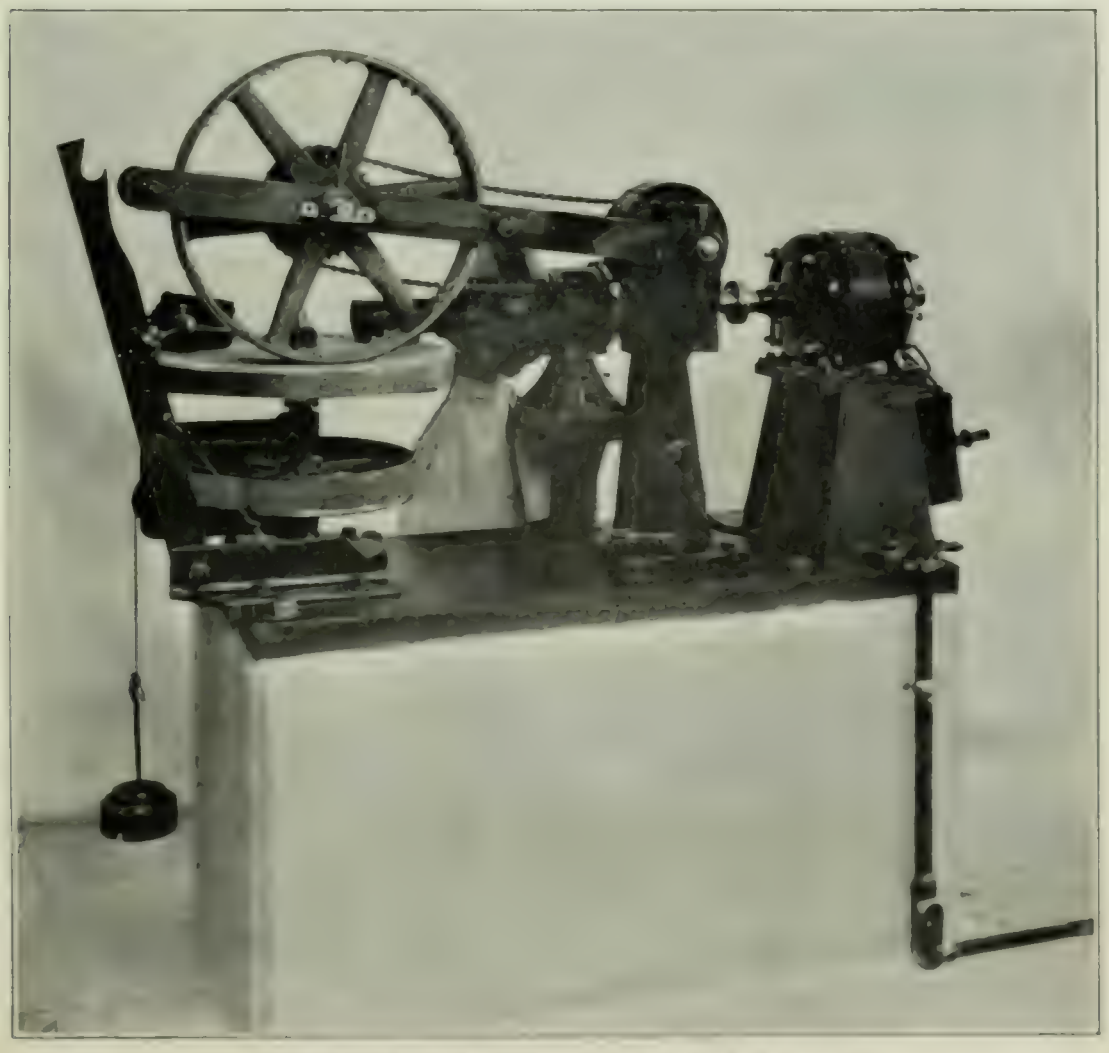

FIG. 2.—*Wearing test machine as used at present*

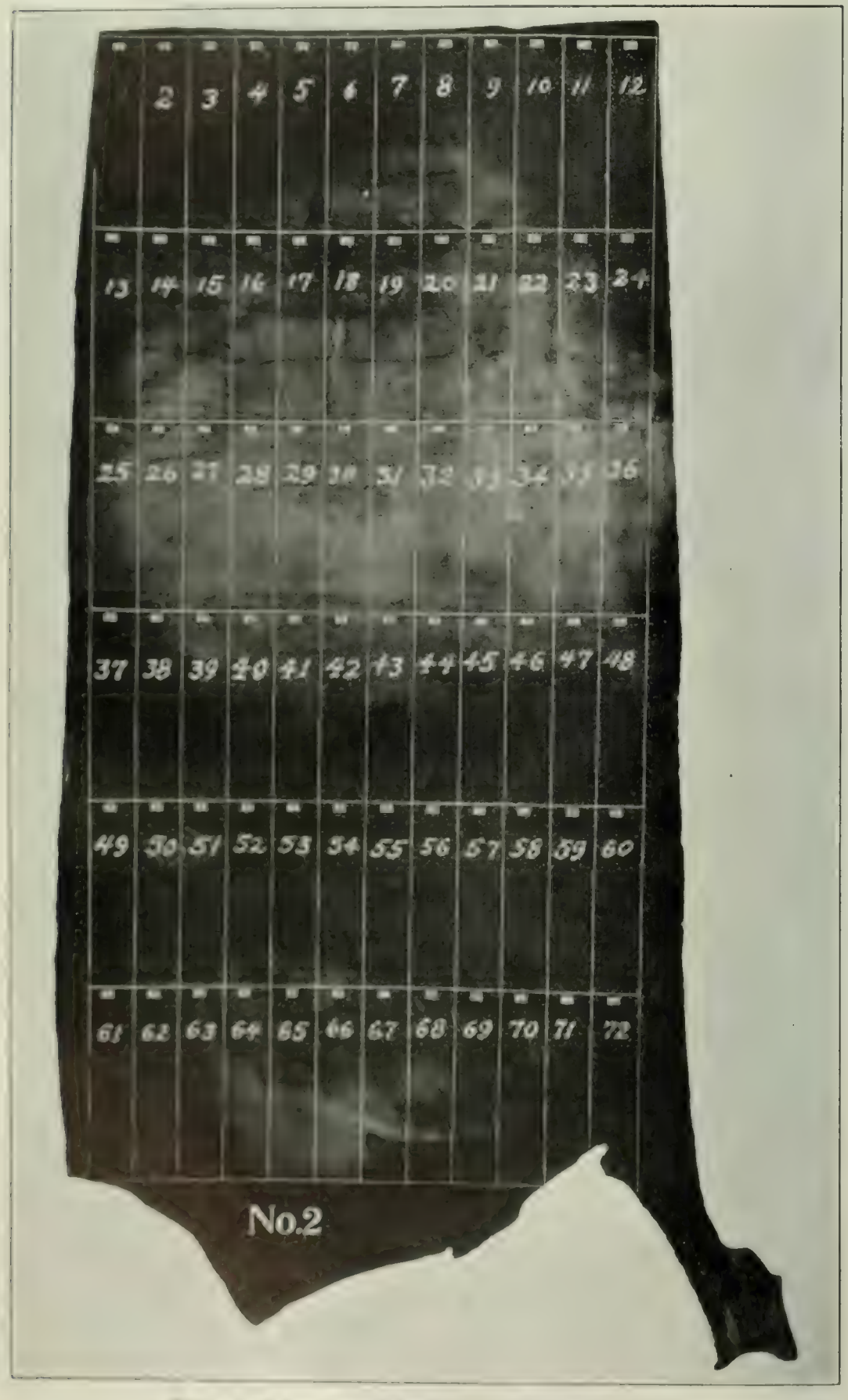


FIG. 3.—*A head marked off for machine wearing test*

A small suction fan and circular brush were added to the equipment in order to remove the dust caused by abrasion. These improvements permitted the wearing conditions to be more uniformly maintained.

## III. METHODS

Sole leather is generally sold in the form of bends. A bend is a half of a hide with the shoulder and belly portions trimmed off, the remaining portion being suitable for soles. In the tests conducted samples of leather from different locations on a bend were used to determine their relative durability or resistance to wear. When a whole bend was tested the general scheme was to divide it into blocks, as illustrated in Fig. 3. Each block was stamped with a code number, which fixed its location on the bend. When using the clover-leaf-shaped cam for holding the samples, test pieces approximately 24 by 5 cm were required and they were attached to the cam by a clinching device. Test pieces for use with the wheel were about half as long and were attached by means of four countersunk screws. In either case the samples were first weighed and then placed on the machine. After the test was completed the samples were again weighed and the loss in weight determined. The relative durability was obtained by determining the loss in volume from the loss in weight and the specific gravity. The sample showing the greatest loss in volume was considered as the least durable.

A small sample adjacent to the test specimen was used in determining the specific gravity. Since only the grain portion was worn away during the test, it was thought desirable to use the specific gravity value for the grain portion only. Accordingly the flesh portion of the sample was removed and the grain portion was then coated with cellulose nitrate to render the sample waterproof. The determinations were then made using a direct-reading gravitometer (Fig. 4).

## IV. RESULTS OF TESTS

*Test No. 1.*—This series of tests was conducted on an oak-tanned bend using the machine with the clover-shaped cam to carry the samples and an abrasive disk of cement. The length of the test was 40 000 revolutions except that in some cases one of the test pieces was entirely worn through before the 40 000 mark was reached; in these cases the machine was stopped and the results figured on a proportional basis.

The four pieces tested at the same time were all taken from the same column across the bend and equidistant from each other so that each run gave an indication of the relative wear across the bend. The exact location of each test piece is shown in Fig. 3.

The results show that in general the resistance to wear is greater at the backbone edge and decreases gradually toward the belly edge of the bend. This is shown in Fig. 5. In studying these results it should be remembered that the best wearing portions of the bend are represented by the lowest points on the curves. In

FIG 4.—*Direct reading gravitometer*

diagrams *B*, *C*, and *D* the results of each individual run may be distinctly seen as one continuous curve, and the general tendency in regard to the wear as stated above is shown in each case. In diagram *A*, all the points in the other three diagrams are plotted, which gives a broken curve, showing that tests of practically the same material made at different times did not check. This failure of the machine to check itself caused the changes previously discussed to be made.

*Test No. 2.*—A scoured oak bend was used in this series of tests. The samples in this case were 10 by 5 cm. in size, and when placed

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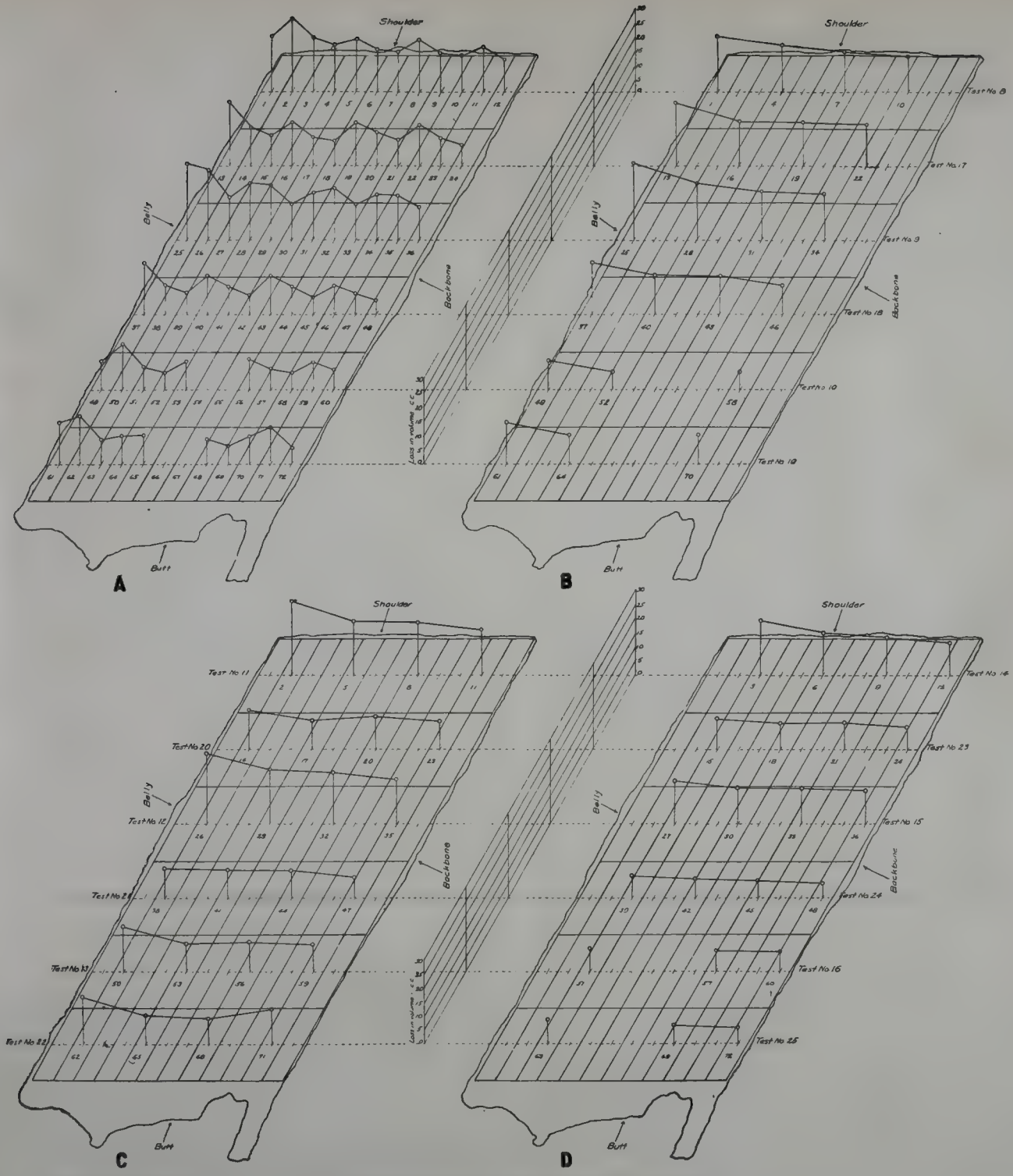


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FIG. 5.—*Results of test No. 1 (ordinates indicate loss in wearing tests)*

on the wheel were made to an apparent even thickness by backing the thinner ones with sheets of metal so that the outer circumference of the wheel, after all the test pieces were in place, presented a smooth surface. Twelve pieces were tested at one time. The same general scheme of placing the samples on the machine for this test was carried out as in Test No. 1.

The results of the tests are given in Fig. 6 and show that the best wearing portions of the bend are along the backbone edge and

FIG. 6.—*Results of test No. 2 (ordinates indicate loss in wearing tests)*

over the kidney. The resistance to wear decreases as the belly edge is approached and also toward the shoulder end of the bend.

*Test No. 3.*—Test No. 3 differs from the preceding test mainly in the fact that the leather was of hemlock tannage instead of oak tannage, and that the conditions of pressure and shear were changed, so that no comparison can be made between the relative wear of the oak and hemlock tannages. The tests were made along the bend with samples of composition material placed alternately on the machine with the leather. The general tendency of the decreasing resistance to wear as the belly edge and the shoulder end

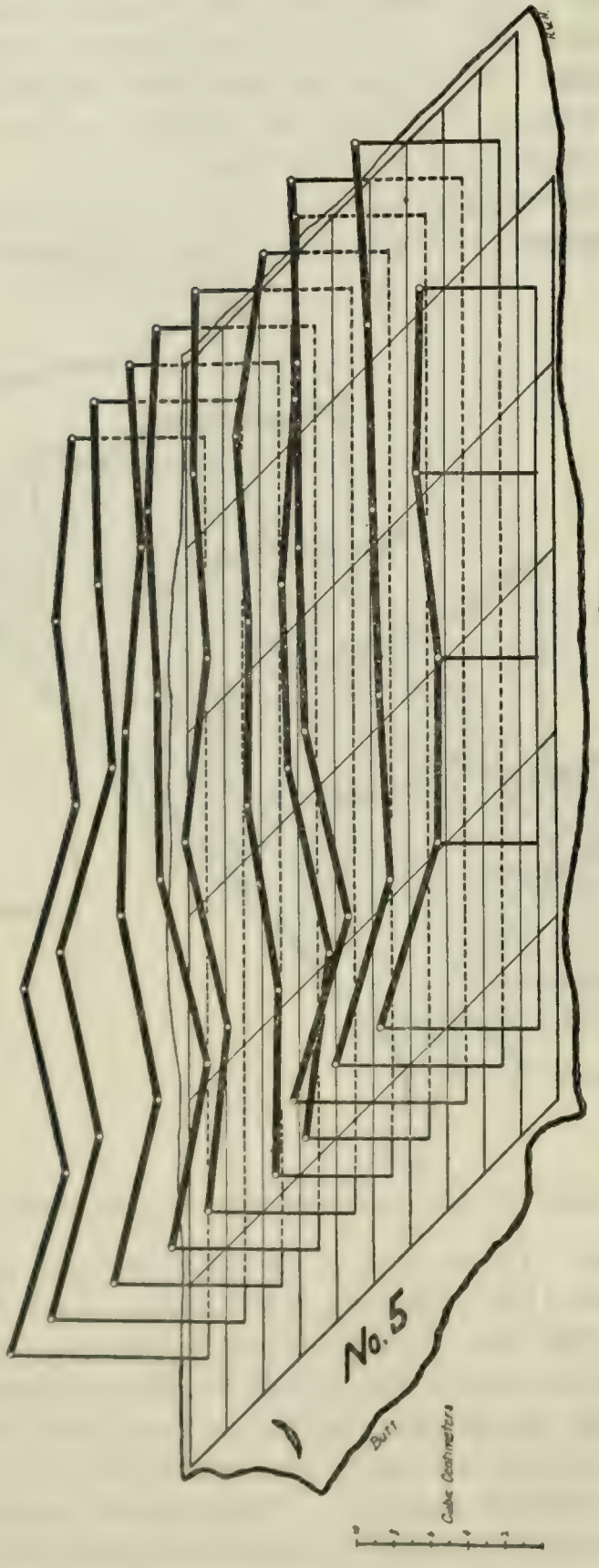


FIG. 7.—*Results of test No. 3 (ordinates indicate loss in wearing tests)*

are approached is shown in Fig. 7. This test also shows that the portion on the extreme butt end near the tail is inferior in wearing quality.

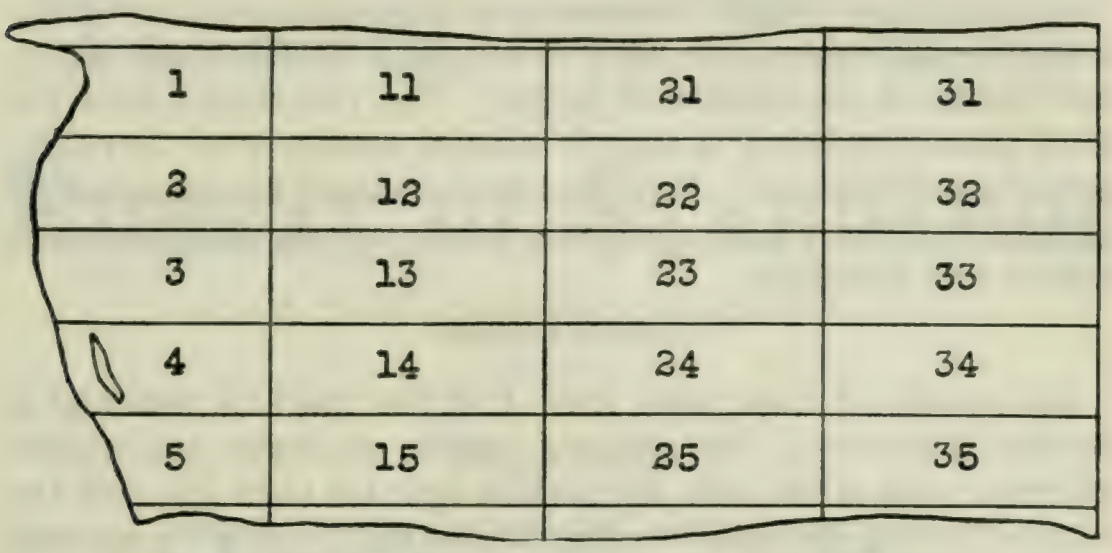


FIG. 8.—*Method of dividing a bend for service and machine tests*

*Test No. 4.*—Several bends of sole leather were divided into blocks as shown in Fig. 8. From each block a sole was cut which was used in an actual service test. A sample for the wearing-test

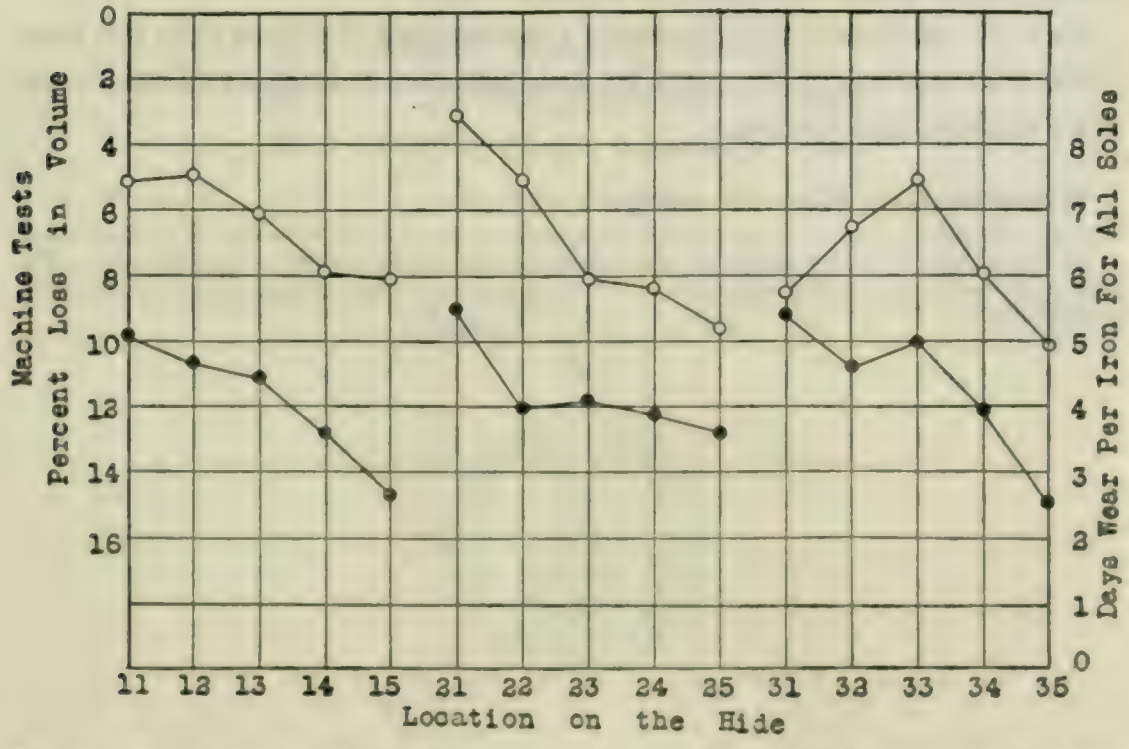


FIG. 9.—*Chart showing relation between actual service tests and laboratory machine tests in test No. 4*

machine was also secured from each block adjacent to the toe end of the sole. A comparison of the results obtained in service and on the machine is shown in Fig. 9.

The upper curve represents the average wear in days per iron[1] for all the soles from each location. The lower curve represents the wear as indicated by the machine tests expressed as the average loss in volume of the test pieces as compared with a standard specimen of composition material, a sample of which was tested with each group of six samples of leather. The two curves show the same general tendency as regards wearing quality with the exception of location No. 31. No cause can be assigned for this apparent discrepancy, but it is expected that subsequent investigations will correct this difference.

## V. CONCLUSIONS

The results of these tests show that the machine indicates a decided difference in the wearing quality of leather taken from different parts of the hide, the portion near the back and over the kidneys having the best wearing quality and those portions near the belly edge, shoulder end, and extreme butt end having considerable less durability. These indications are in accord with the opinion and experience of many tanners and leather manufacturers. The results obtained on the machine in Test No. 4 also agree quite closely with those obtained in service tests.

In view of these facts it seems reasonable to believe that the machine may properly be used to indicate the relative resistance to wear of different leathers.

WASHINGTON, May 26, 1919.

[1] The iron is a unit of measure used in the leather trade to designate the thickness or gage of leather and is equal to approximately one-half millimeter in the metric scale, and equal to one forty-eighth inch in the English scale.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

## No. 148

## THE ULTRA-VIOLET AND VISIBLE TRANSMISSION OF VARIOUS COLORED GLASSES

BY

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*Bureau of Standards*

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# THE ULTRA-VIOLET AND VISIBLE TRANSMISSION OF VARIOUS COLORED GLASSES

By K. S. Gibson, E. P. T. Tyndall, and H. J. McNicholas

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Methods and accuracy | 4 |
| III. Transmission data | 6 |
| 1. Definition of terms | 6 |
| 2. Nearly neutral glasses | 8 |
| 3. Didymium glasses | 9 |
| 4. Red glasses | 10 |
| 5. Orange and yellow glasses | 11 |
| 6. Green glasses | 12 |
| 7. Blue-green glasses | 13 |
| 8. Blue glasses | 13 |
| 9. Purple glasses | 14 |
| 10. Applications | 15 |
| 11. Monochromatic light filters | 19 |
| IV. Summary | 20 |
| Appendix | 26 |


## I. INTRODUCTION

During the last three years the spectral transmissions of a great number and variety of glasses have been measured by the Bureau of Standards throughout the ultra-violet, visible, and infra-red. The transmissions throughout the infra-red, and extending into the visible, have already been published,[1] as well as the transmissions for the visible and ultra-violet of glasses particularly classed as eye-protective.[2]

In the present paper are given the transmissions for the visible and ultra-violet of a large number of glasses, mostly colored, which are not used primarily for eye protection, but which are useful for various other purposes. These data have been accumulating for the last three years; and it was thought worth while to publish those which might be of value or interest to others, without,

[1] Coblentz and Emerson, B. S. Technologic Paper No. 91; May, 1917; 2d ed., February, 1919. Coblentz, Emerson, and Long, B. S. Scientific Paper No. 472; August, 1918.

[2] Gibson and McNicholas, B. S. Technologic Paper No. 119, June, 1919.

however, trying to make an exhaustive report on all the possible glasses obtainable.[3]

The glasses listed in this and the other papers mentioned, however, are representative of what may be obtained to-day on the American market, and include also some of foreign make which could be obtained before the war. It is thus possible to make comparison of the relative merits of foreign and American glass and see in what respects the latter may duplicate or improve upon the former.

Although many transmission data are on file on substances other than glass, these are not included in this paper, being reserved for the future, when more complete data can be presented. Moreover, certain kinds of glasses, such as "Lovibond tintometer" glasses, artificial-daylight glasses, and present-day standard railway-signal glasses, are not included in this paper, inasmuch as such data are to appear in separate papers on these particular subjects.

Very little previous work on the ultra-violet transmission of colored glasses, excepting those classed especially as eye-protective, has been published. Previous publications of transmissions throughout the visible include a paper by Gage,[4] of the Corning Glass Works, in which the principal coloring constituents of many of the glasses herein listed are given, and papers by Gibbs[5] and Gibson,[6] in which the change in the transmission with temperature is given for many glasses similar to those of this paper.

## II. METHODS AND ACCURACY

Photographic, photoelectric, and visual methods were used in obtaining the data herein presented. Some of the photographic and visual determinations were made in the physical laboratory of Cornell University in 1917, and thanks are due to Prof. E. L. Nichols, of Cornell, for placing the facilities of that laboratory at the Bureau's disposal.

Photographic determinations were made by the Hilger sector-photometer method with a quartz spectrograph. At Cornell the apparatus was used as set up and described by Howe[7] (width of slit of spectrograph =0.15 mm). During 1917 a duplicate of the

[3] The authors have had the assistance of J. M. Hyatt, J. T. Pilgate, and H. E. Cole in obtaining part of the data herewith given. The tracings were made by C. L. Snow.

[4] Trans. I. E. S., 11, p. 1070, 1916.

[5] Phys. Rev., 31, p. 460, 1910.

[6] Phys. Rev. (2), 7, p. 151, 1916.

[7] Phys. Rev. (2), 8, p. 674; 1916.

sector photometer was constructed in the Bureau's instrument shop, and since February, 1918, measurements have been made here by this method (slit width = 0.10 mm). Certain minor changes and refinements have been made in the method, however. These are described in the Appendix.

The photoelectric method is the null method described in a recent paper [8] (slit width = 0.20 mm) and has been in operation since April, 1918.

Three visual methods were employed. At Cornell the Lummer-Brodhun spectrophotometer was used. Only a few of the specimens were measured on this instrument.

By far the greater part of the visual data given in this paper were obtained on the König-Martens spectrophotometer [9] at the Bureau (slit width = 0.10 mm). This has been in use here since 1912. The apparatus at present employed for illumination of the König-Martens spectrophotometer field may be described as follows: [10]

1. The light sources are inclosed in a white-lined diffusing box. There are receptacles in the box for ten 500-watt, gas-filled, tungsten lamps and space for three large mercury lamps.

2. The spectrophotometer is so placed as to "look into" this box through suitable diaphragmed apertures in one end of it, so that the illumination of the field is obtained from diffusely reflecting surfaces on the inside of the opposite end.

3. In measuring transmission the surfaces illuminating the field are both white (magnesium oxide or carbonate) and the sample intercepts the light from one of the surfaces in the space between the slits and the outside of the box.

4. In measuring reflection the sample is substituted for one of the white surfaces.

5. Both reflection and transmission measurements are made by the method of interchanging sample and standard before the two slits, and means are provided for doing this quickly and conveniently.

6. The illumination box is cooled by the circulation of water in an inclosing jacket.

In addition to the above methods the Martens photometer [11] is used considerably at the Bureau, with a mercury arc as source.

---

[8] K. S. Gibson, B. S. Scientific Paper No. 349, October, 1919.

[9] Ann. d. Phys. (4), 12, p. 984, 1903.

[10] Design by Irwin G. Priest and H. J. McNicholas. To be described in detail later in B. S. Technologic Paper.

[11] Phys. Zeit., 1, p. 222, 1900.

By means of suitable selective ray filters (Fig. 23), the violet, blue, green, and yellow lines can be isolated and accurate check readings taken at these wave lengths.

A brief description of the method of use of the Hilger sector photometer, the Lummer-Brodhun spectrophotometer, the König-Martens spectrophotometer, and the Martens photometer is given in Bureau of Standards Technologic Paper No. 119. For further details, the original papers should be consulted.

All of the glasses, so far as it was possible to get values, were measured photographically and visually, and in most cases photoelectrically. The methods overlap to such an extent that when all are used extremely reliable transmission curves may be obtained. The photographic method may be used from 230 to 500 millimicrons (m$\mu$), the photoelectric from 380 to 600 m$\mu$, and the visual from 436 to 720 m$\mu$. This overlapping is sufficient to eliminate the uncertainty which always appears as the limiting regions for any method are reached.

With possibly a few exceptions, therefore, the curves as given in this paper are considered accurate within 2 units, considering the transmission scale of 0.00 to 1.00 as being divided into 100 units; and in many cases, especially at low transmissions and in the better specimens, the uncertainty is definitely less than this. The actual values have not been plotted, inasmuch as the purpose of the paper is to give information as to the transmission rather than to compare methods, and the values, if plotted, might cause considerable confusion.

## III. TRANSMISSION DATA

### 1. DEFINITION OF TERMS

The transmission of a specimen is defined as that fraction of radiant energy incident on the first surface which gets through the second surface. In a comparison of the transmissions of different samples, due account must be taken of the variation of transmission with thickness. This may be done, at least approximately, by means of the following equation:

$$\mathrm{T} = \frac{T}{(1-R)^2} = t^b,$$

wherein $T$ is the transmission as already defined, $R$ is the fraction of radiant power reflected at each surface of the specimen, T is the transmittance or the transmission corrected for reflection, $b$

SES b'/b

REQUIRE

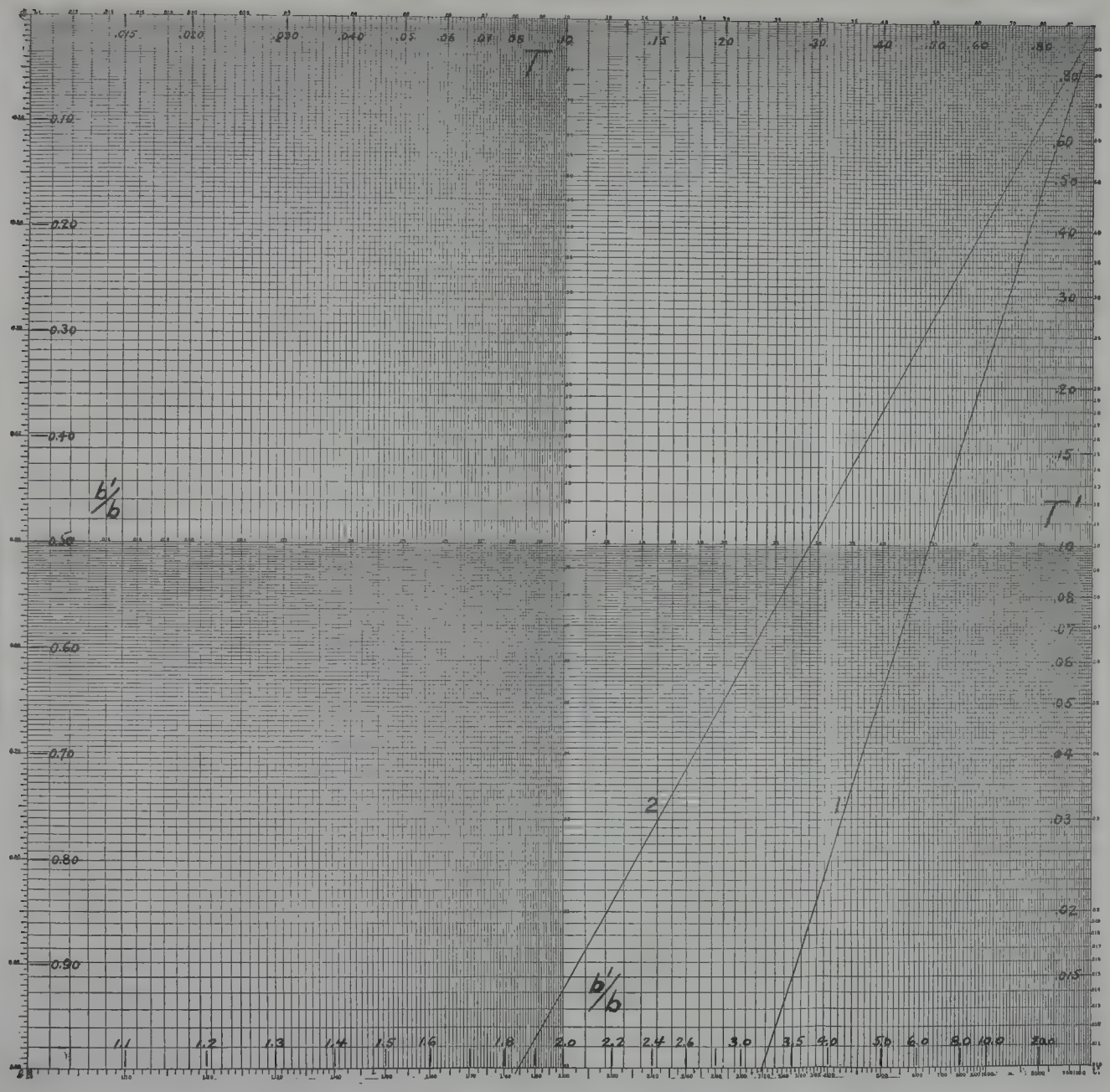


FIG. 1—*Reproduction of chart used at Bureau of Standards for computing transmissions for different thicknesses and vice versa*

*Method of use.*—To find $T'$ when $b'$, $T$, and $b$ are given: Lay a straight edge from origin in upper right-hand corner to value of $b'/b$ found on left-hand or lower scale. Find T ($=T/0.92$) on upper scale and follow it down to intersection with the straight edge. The value of T ¹ on right-hand scale corresponding to this intersection is the required transmittance and $T'=0.92$ T'. Example (Line 1): Given $T=0.50$ and $b=1.68$ mm; to find $T'$ when $b'=1.37$ mm.

To find $b'$ when $T'$, $T$, and $b$ are known: Lay a straight edge from upper right-hand corner through the intersection of T and T' ($=T/0.92$ and $T'/0.92$, respectively). The intersection of this straight edge on the lower scale gives $b'/b$, from which $b'$ can be found. Example (Line 2): Given $T=0.50$ and $b=1.68$ mm; to find $b'$ when $T'=0.30$.

141646°—20. (To face page 6.)

is the thickness between surfaces, and $t$ is the transmissivity or transmittance per unit of thickness. This computation of the transmissions for different thicknesses or the thicknesses corresponding to different transmissions may be easily carried out

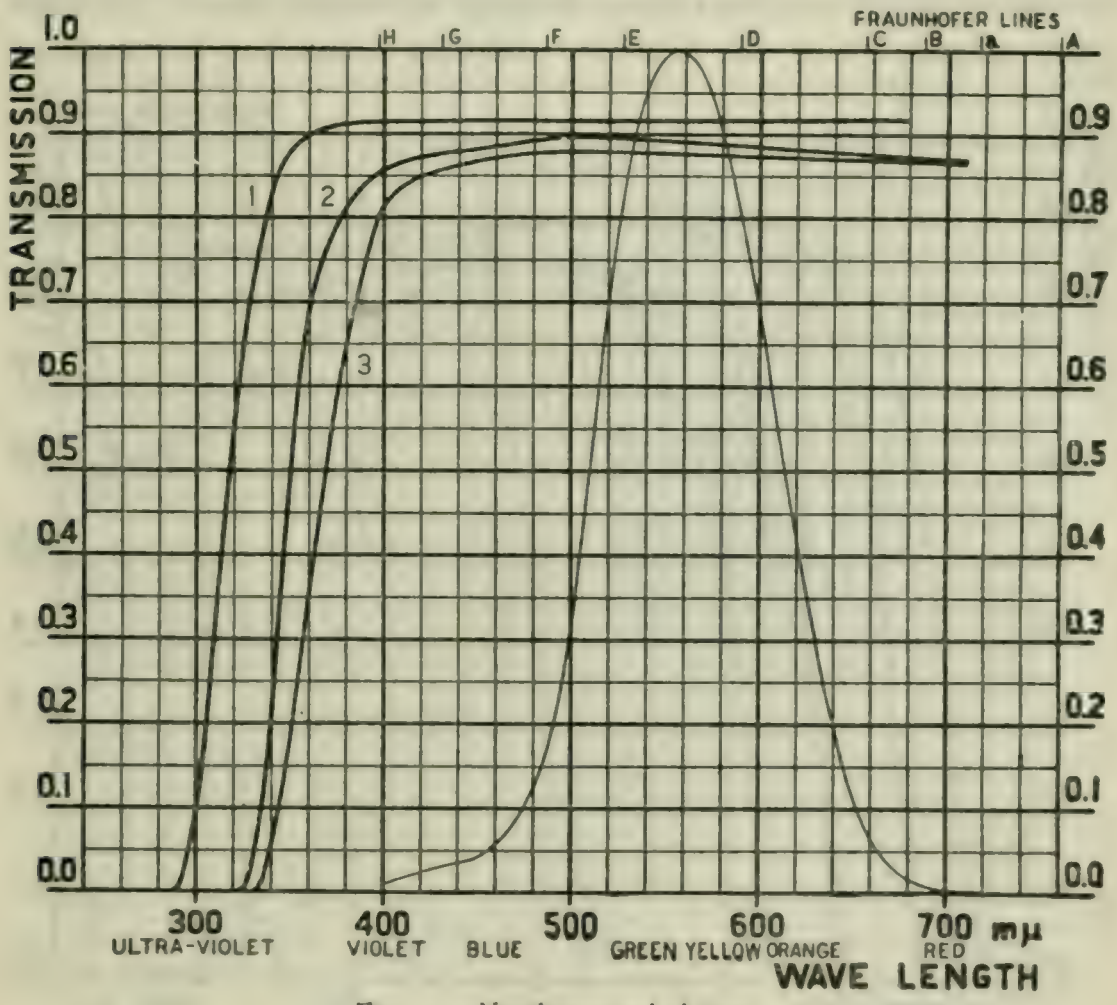


FIG. 2.—*Nearly neutral glasses*

1="Crown 1.50," 1.68 mm; A. O. Co. 2="G111CD," 8.30 mm; 3="122BR," 8.04 mm; C. G. W.

graphically, as illustrated in Fig. 1, which is a reproduction of the chart in use at the Bureau.[12]

The transmission data are shown by the curves in Figs. 2 to 21, the specimens and curves being numbered (from 1 to 87) for convenient reference. For each specimen, the maker or dealer,[13] the trade name or designation, and the thickness are given in the

[12] Same chart as that in B. S. Tech. Paper No. 119, Fig. 25. The original of this chart was designed at the Bureau in 1915 for this particular kind of work. The chart from which this published figure was copied was ruled by Keuffel & Esser according to this design. It was subsequently called to our attention that Luckiesh and Cady (Trans. I. E. S., IX, p. 853, 1914) had used a somewhat similar chart; but in its published form this is too small to be of practical value to the reader, except as an illustration of the method. The large reproduction of the Bureau's chart has been given in the hope that the reader could actually use it in the solution of problems similar to those illustrated.

[13] A. O. Co.=American Optical Co., B. & L.=Bausch & Lomb Optical Co., C. G. W.=Corning Glass Works, Jena=Schott & Gen., Glaswerk, Jena.

legends. In many cases curves are given for more than one thickness of glass of a given name. In the case of the Jena precision samples and others, these different thicknesses were cut from the same part of the same glass, but in some cases different samples of the same name were cut from entirely different stock. In each figure also is given the relative visibility curve for the average

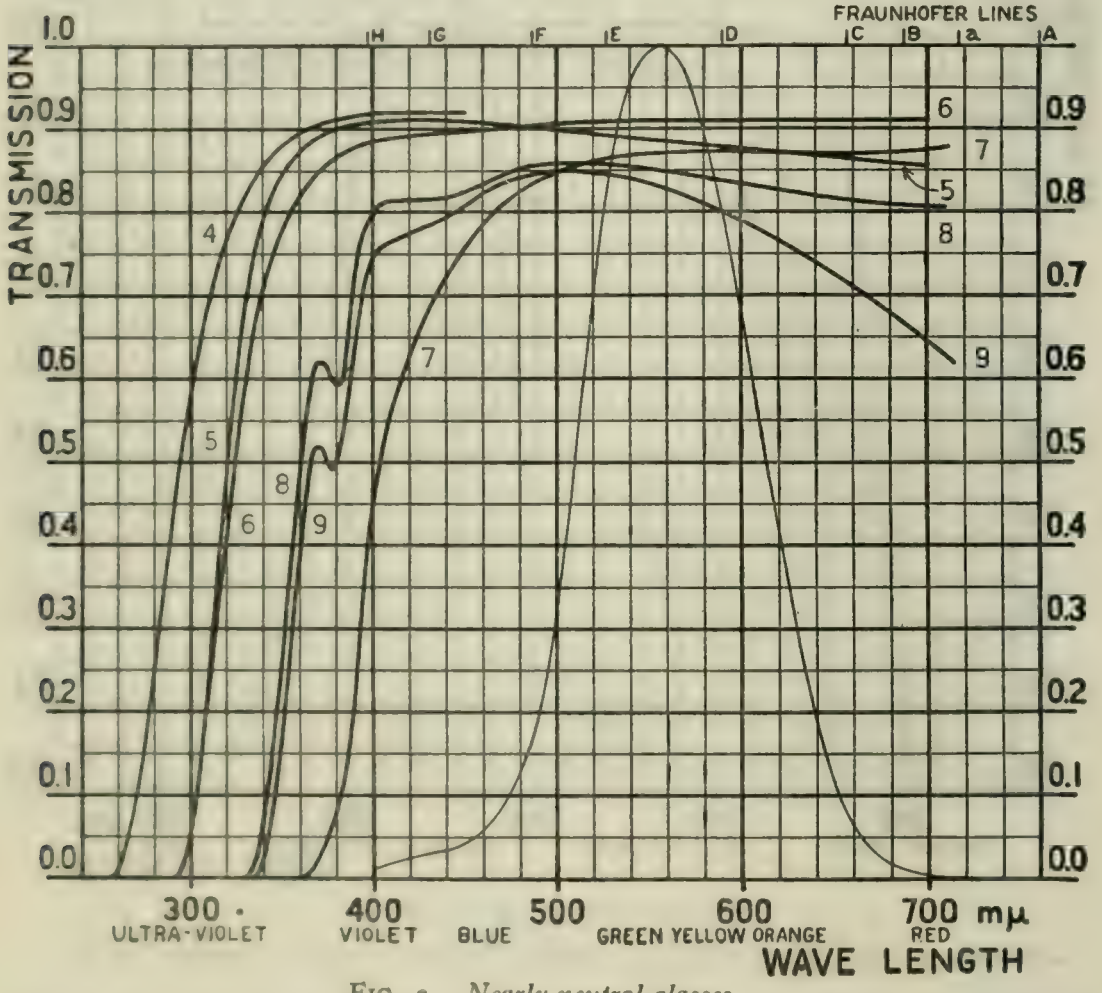


FIG. 3.—*Nearly neutral glasses*

4="G123S Ultra," 2.49 mm; 5=same, 3.49 mm; 6="Pyrex," 0.77 mm; 7="G123N Nultra," 4.84 mm; C. G. W. 8 and 9=mirror glass, 21.01 mm and 19.54 mm; B. & L.

human eye as obtained at the Bureau.[14] Inasmuch as an inspection of the curves will give practically all the information desired, little need be said in discussion except to call attention to certain points of special interest or importance.

## 2. NEARLY NEUTRAL GLASSES

The Corning "Ultra" glass, curves 4 and 5, is of special interest, for it transmits farther into the ultra-violet than any other neutral glass so far examined. Its ultra-violet transmission is very

[14] Coblentz and Emerson, B. S. Scientific Paper No. 303; September, 1917.

similar to that of the blue glasses shown by curves 64 and 68, the thin sample transmitting about 1 per cent even at 260 mμ. The sample "G123N Nultra" has practically the same transmission as the "Noviol O" samples, whose curves are given in Bureau of Standards Technologic Paper No. 119. The "Pyrex" glass is

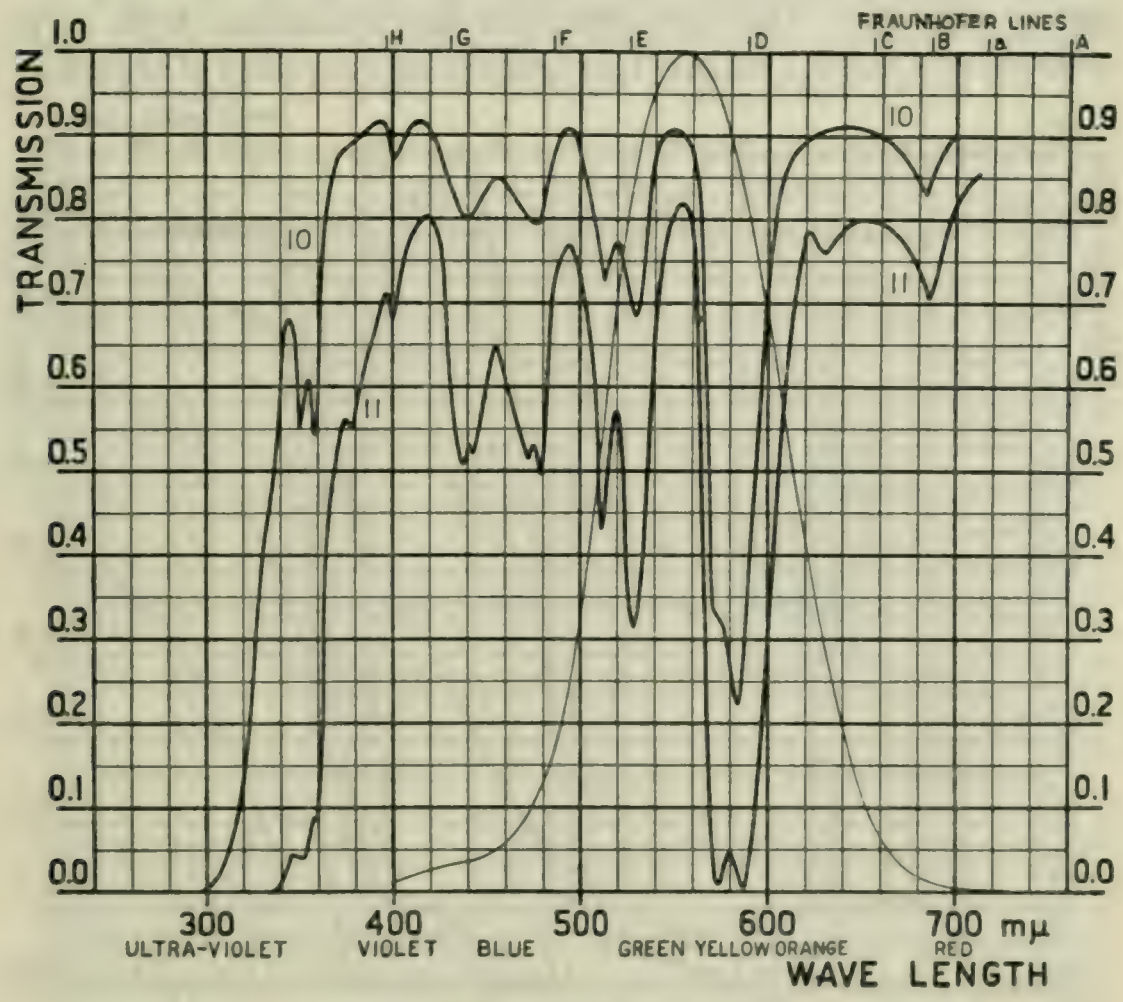


FIG. 4.—*Didymium glasses*

10="3728," 5.22 mm; Jena. 11="G555P," 3.02 mm; C. G. W.

notable for its low thermal expansivity and its extensive use in chemical and cooking glassware.

### 3. DIDYMIUM GLASSES

These glasses, Fig. 4, are remarkable for the large number of strong and narrow absorption bands. The Corning and Jena samples are very similar, although, as may be noted at wave lengths 350–390, 570–590, and 630 mμ, they are not exactly alike. This glass is of special value as a ray filter for use with the mercury arc, for it absorbs the yellow lines very strongly, while transmitting the green quite freely. Its absorption of the helium, sodium, and other yellow lines is also of value in special cases.

### 4. RED GLASSES

The curves of Fig. 5 show the transmissions of two kinds of Jena red glass at different thicknesses. These and the other Jena glasses, except specimens 10, 48, 64, and 65, comprise a set of standard precision glasses kept on file at the Bureau for the purpose of comparing methods. They are especially fine specimens, both as to material and finish, and any discrepancies in the values of the trans-

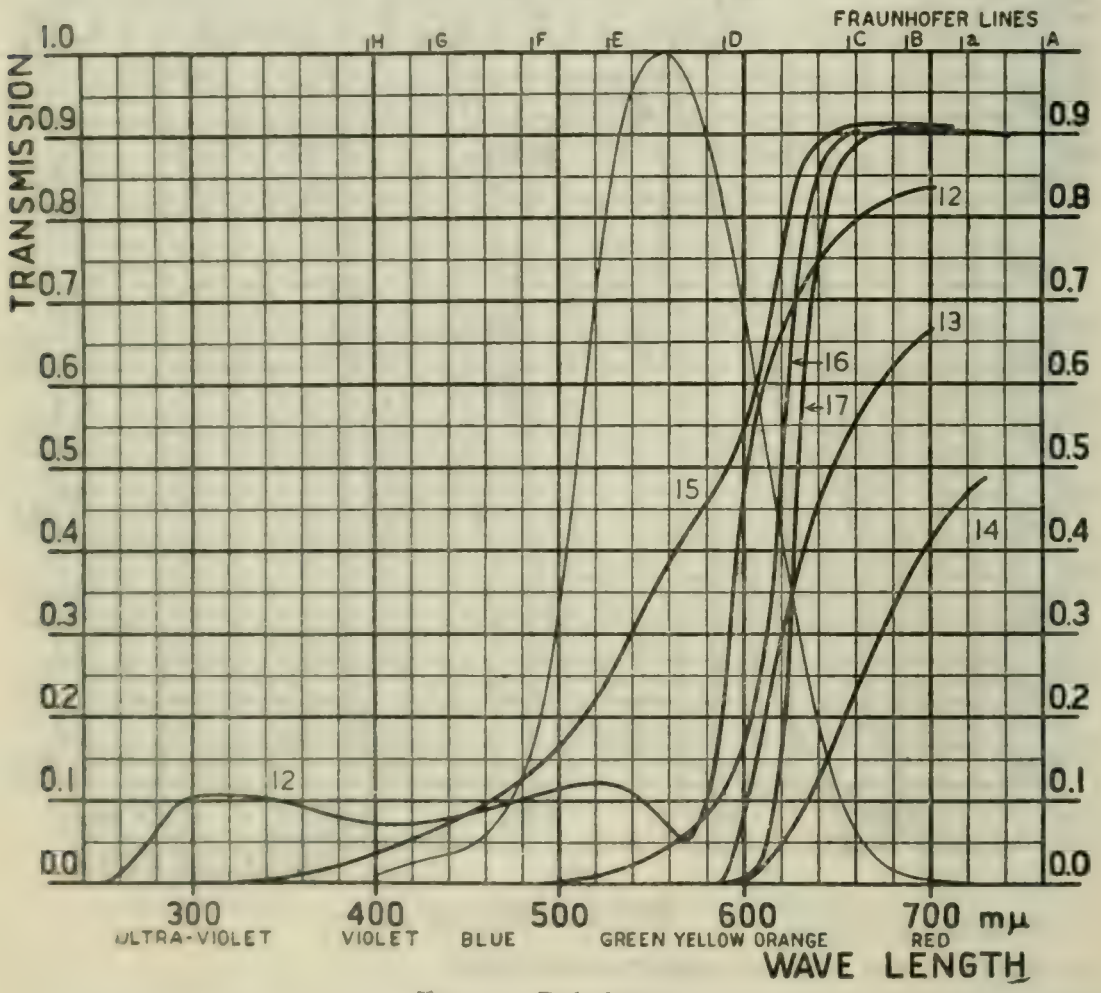


FIG. 5.—*Red glasses*

[illegible] mm; 14=same, 2.90 mm; 15="4512," 0.30 mm; 16=same, 1.02 mm; [illegible] mm, Jena.

mission by different methods can be laid entirely to the method, and not to the specimen. Specimen 12 is remarkable for its transmission of the ultra-violet, though nominally a red glass, and the curve illustrates how little can be told regarding the transmission of thin specimens from that of a thicker one of the same kind.

The Corning glasses of Fig. 6 are similar to Jena "4512". They do not have as high transmission in the red, but the transmission is much more sharply reduced to an inappreciable amount than in the Jena glasses. For most purposes, the Corning red

would probably be more desirable than the Jena. It is understood that Corning red glass can now be obtained of higher transmission than that found for these samples.

### 5. ORANGE AND YELLOW GLASSES

In Fig. 7 are given curves for different shades of Corning "G34" and "G38 Noviol". Curves for a large number of other "Noviol" glasses are given in Bureau of Standards Technologic Paper No. 119.

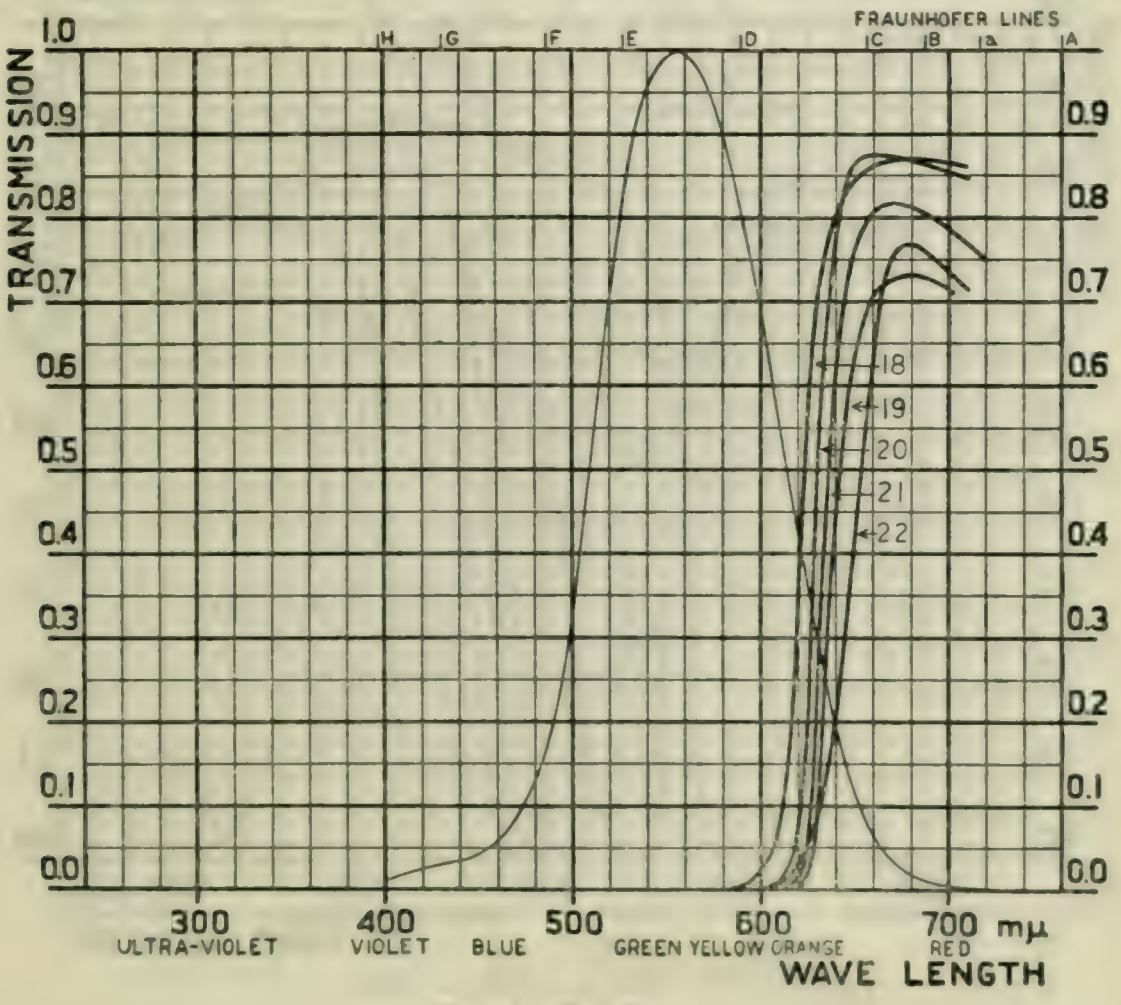


FIG. 6. – *Red glasses*

18 = "G24," 6.98 mm; 19 = same, 5.97 mm; 20 = "Ruby 100%," 0.50 mm; 21 = same, 4.18 mm; 22 = "G20," 7.2 mm; C. G. W.

Most of these glasses are characterized by the sharp transition between high transmission and strong absorption, and are used to absorb ultra-violet, to eliminate haze and thus improve visibility both in visual and photographic work, and, in general, as selective ray filters. Different samples of this kind vary greatly in the sharpness of the transition between absorption and transmission and in the value and shape of the curve where the transmission is high.

In Figs. 8 and 9 are given curves for other samples of orange and yellow glass, these being the usual shades of the different kinds, while the various shades of "G34" in Fig. 7 were made on a special order.

The Jena glass of Fig. 10 is similar in appearance to the deep shades of "Noviol," but has a more uniformly high transmission in the red, yellow, and green, and a very gradual decrease in

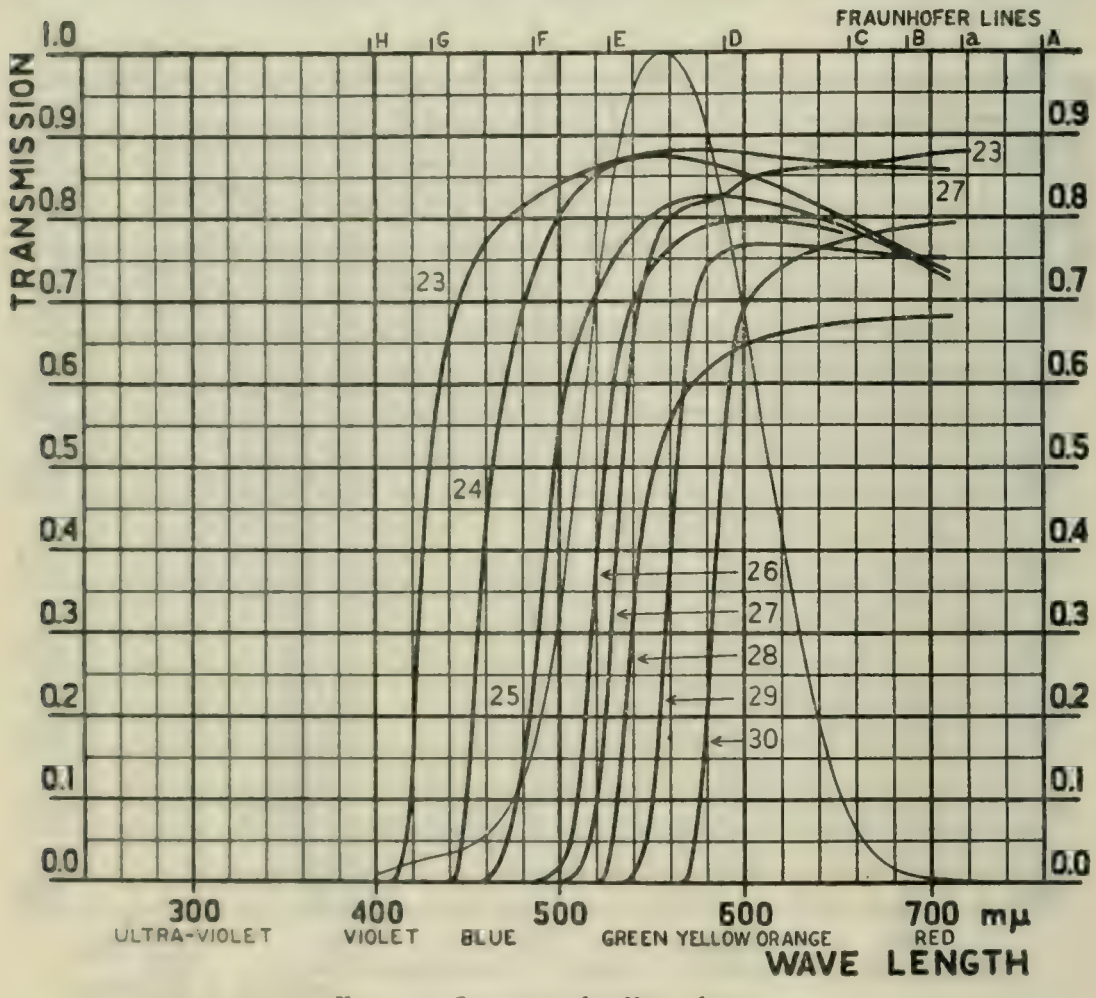


FIG. 7.—*Orange and yellow glasses*

23="Noviol A," 2.02 mm; 24="G38 Noviol B," 3.22 mm; 25="G38 Noviol C," 4.23 mm; 26 to 30=special shades of "G34," 26=2.25 mm; 27=0.93 mm; 28=3.68 mm; 29=3.45 mm; 30=3.16 mm; C. G. W.

transmission through the violet and ultra-violet. It therefore has not the value for most purposes that the "Noviol" has.

The glasses of Fig. 11 are fluorescent. This kind is quite commonly called "canary" glass and fluoresces with a greenish light. The Jena and Corning samples seem to be practically the same.

### 6. GREEN GLASSES

In Fig. 12 Jena and Corning green glasses are compared. They are very similar, although the transmission band of the latter is at slightly shorter wave length than that of the former.

### 7. BLUE-GREEN GLASSES

Various types and shades of blue-green glasses (green by yellow light) are shown in Figs. 13 and 14. This type of glass usually gives very good protection against the infra-red.

### 8. BLUE GLASSES

Three kinds of Jena blue glass are shown in Figs. 15 and 16. Specimens "8780" and "3653" have not been duplicated in any

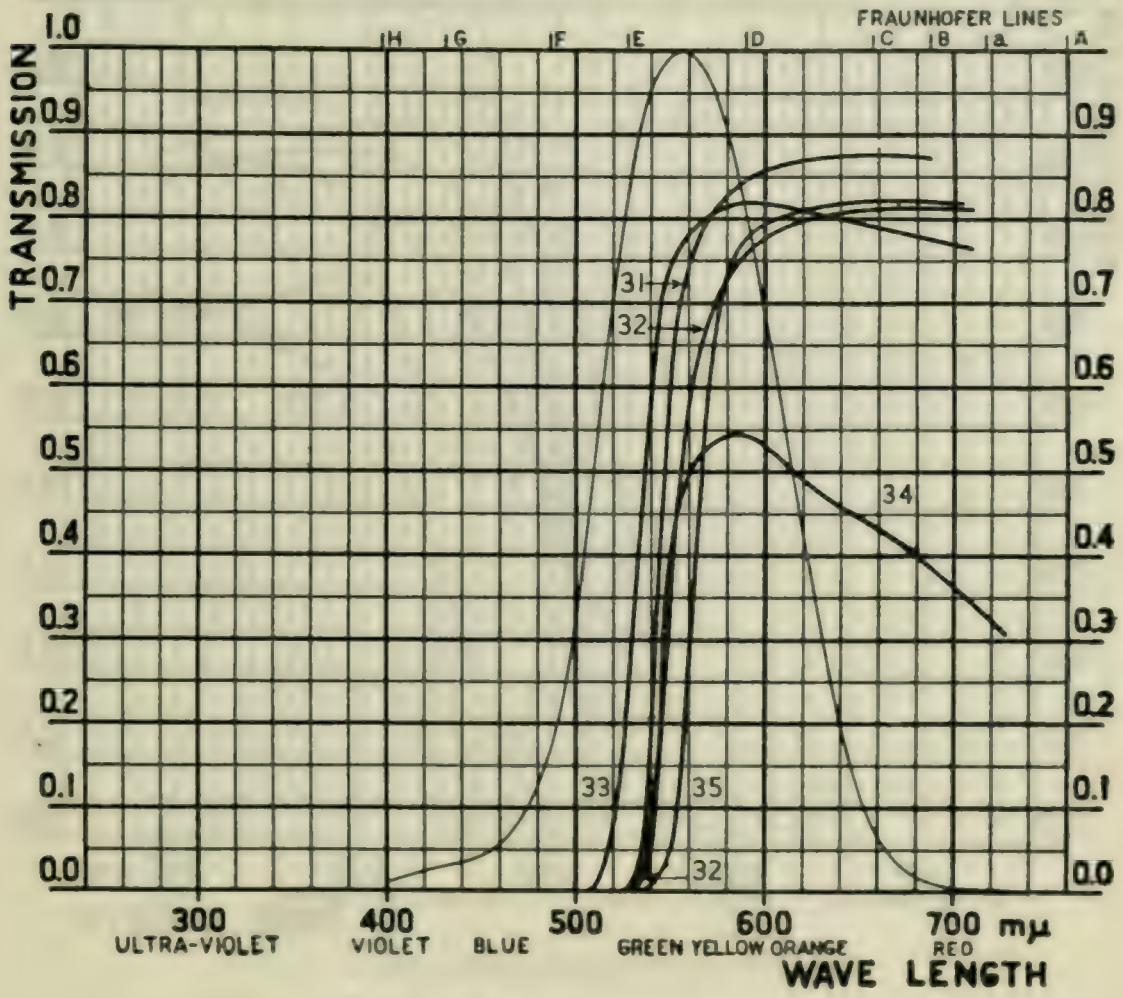


FIG. 8.—*Orange and yellow glasses*

31="G34," 1.50 mm; 32=same, 3.68 mm; 33="G34B 143%," 1.13 mm; 34=same, 6.40 mm; 35="G341F," 2.12 mm; C. G. W.

of the glasses examined. The thick sample of "3653" transmits farther into the ultra-violet than any other glass ever examined, if the curves for these others be reduced to that for a thickness of 5.45 mm. However, the thin specimen transmits no farther than the various other thin specimens which go to about 1 per cent at 260 mμ.

In Figs. 17, 18, and 19 are shown a number of different kinds of Corning blue glass, some of them appearing purple if viewed by

yellow light. "G585", curves 68 and 69, seems to be a duplicate of Jena "3654," Fig. 16.

### 9. PURPLE GLASSES

Purple glasses of lighter and darker shades are shown in Figs. 20 and 21. Those of Fig. 21 are of special interest and value. They are the best obtainable for demonstrating fluorescence, they

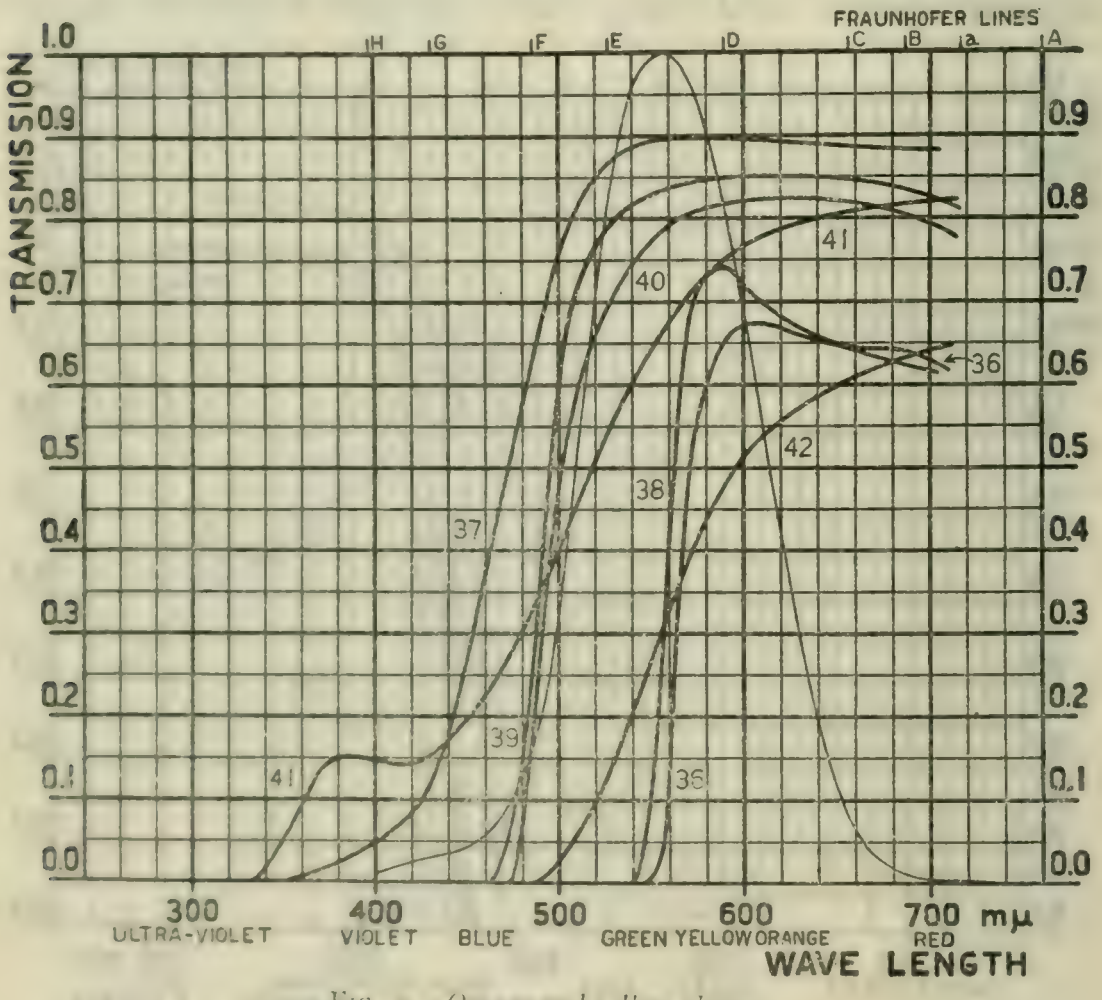


FIG. 9.—*Orange and yellow glasses*

[illegible]; 38=same, 6.51 mm; 39="G36:CE," 3.04 mm; 40=same, [illegible]; 41=same, 4.79 mm; C. G. W.

are of value as selective ray filters, and may be put to other uses. "G586J" and others very similar have been used in ultra-violet signaling.* The red and infra-red transmission of this glass is too small to measure. "G586N" transmits considerably more red than "G586J." It will be noted that the maximum trans-

*"[illegible] Report on the Navy Department, Bureau of Steam Engineering) on the Possibility of [illegible] and the Applicability of Ultra-Violet Radiation to Signaling," by [illegible]. "Report on the Applicability of Ultra-Violet Rays to [illegible]" by Jean G. Priest and K. S. Gibson, Paper communicated to American Physical Society; [illegible]

mission varies from 370 mμ in the lightest shade to 360 mμ in the darkest.

### 10. APPLICATIONS

There are many practical uses to which these glasses may be put, in addition to those already mentioned. Some of them, or somewhat similar glasses, are used in railway signaling; others, alone or in combination, are used to isolate certain parts of the spectrum; and various other ways in which the different types

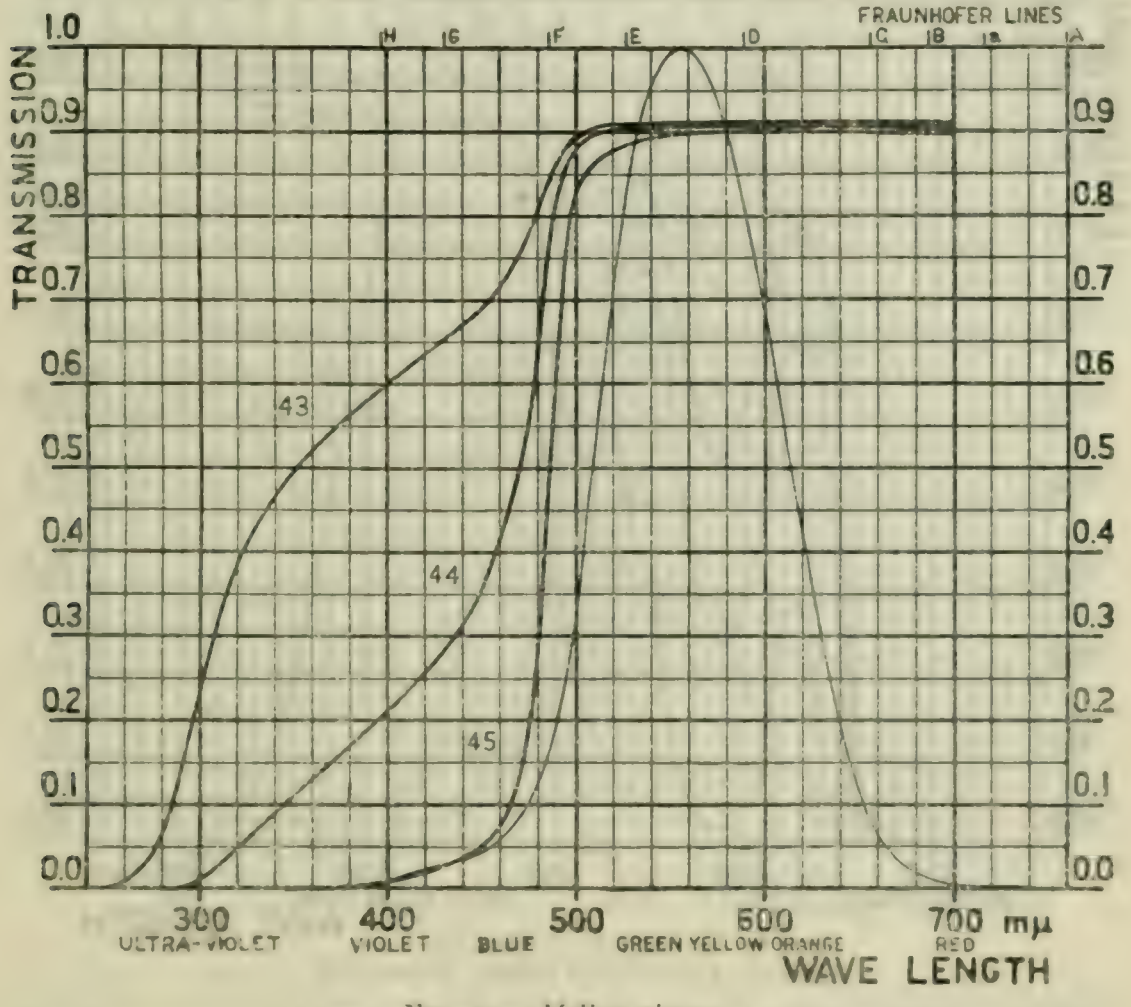


FIG. 10.—*Yellow glasses*

43—"55%," 6.10 mm; 44—same, 1.62 mm; 45—same, 1.22 mm, Jena.

might be used will occur to those interested. Those labeled "Ruby 100%," "Yellow 100%," "Green 100%," "Blue 100%," and "Purple 100%" are samples from old railway-signal glasses, but were not measured through the original surfaces. A paper is now in preparation giving the transmission in the visible of present-day standard railway-signal glasses, precision measurements being made both through the original surfaces and through the same specimens planed and polished, the specimens being cut from the center of the roundel.

As already noted, glasses having a type of curve given in Figs. 6 and 7 are very valuable as photographic ray filters, for improving visibility, or for protecting the eyes from the ultra-violet while transmitting highly in the visible. By varying the thickness it is possible to have the steep part of the curves—that is, the transition between high and low values of transmission—occur at any wave length. The glasses of Figs. 6 and 7 make this possible

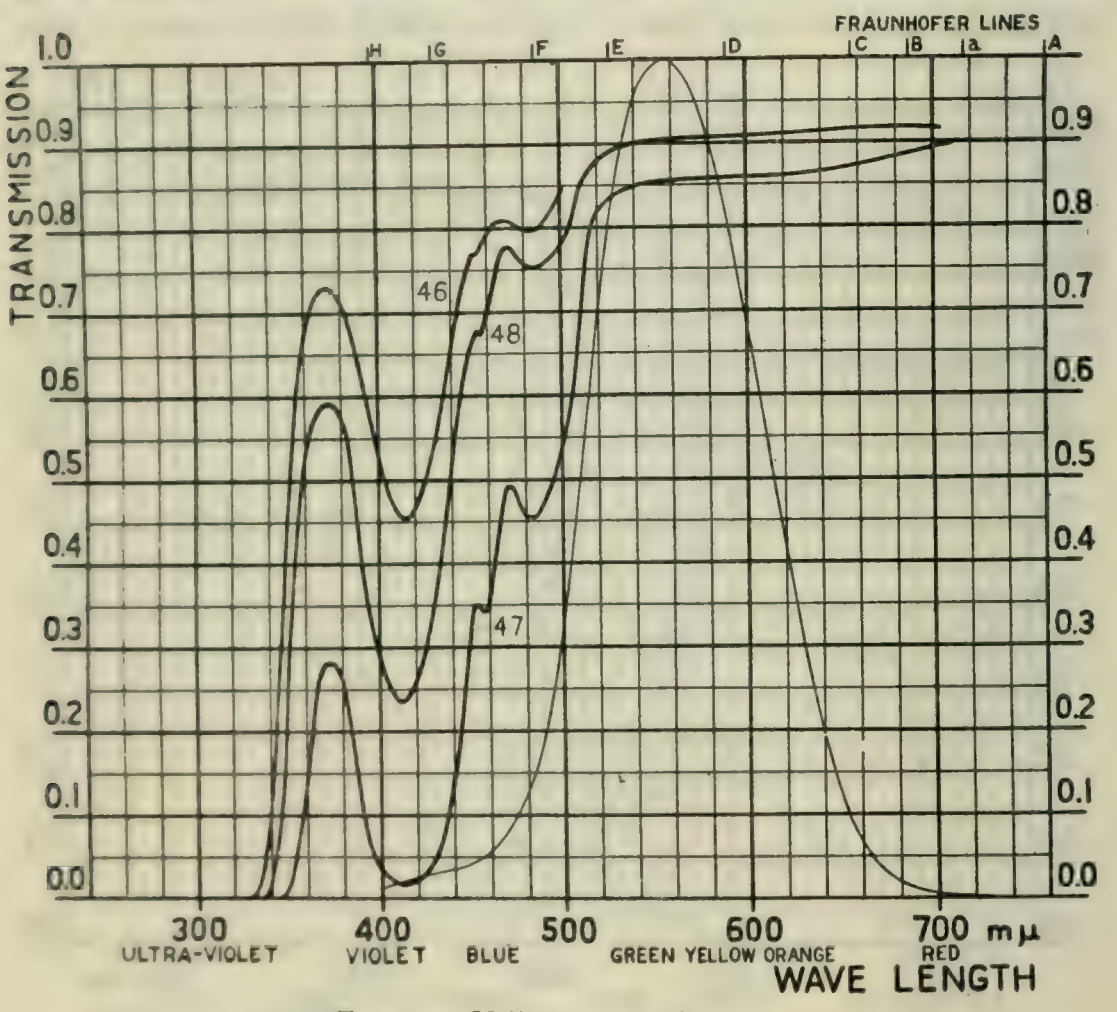


FIG. 11.—*Yellow glasses, fluorescent*

46="G[illegible]," 0.99 mm; 47=same, 5.79 mm; C. G. W. 48="3757," 1.97 mm; Jena.

anywhere from 400 to 660 mμ. By the use of different thicknesses of various neutral glasses, as illustrated in Figs. 2 and 3, this type of curve may be extended into the ultra-violet below 300 mμ. By combining the glasses of Fig. 6 with glasses like 69, 74, and 83, the same type of curve may be obtained from 670 mμ toward the infra-red.

The inverse type of curve—that is, low transmission at long wave lengths and high transmission at shorter wave lengths—may be obtained by some of the glasses shown in Figs. 13 to 21, though

the transition is usually much more gradual. However, if frequencies instead of wave lengths be plotted, this difference is not so apparent.

Some of the glasses of Figs. 12, 14 (curve 58), 15, 16, 17, 18, 20, and 21 make it possible to isolate certain more or less narrow regions of the spectrum, the various maxima occurring at 360, 370, 390 (69×81), 410, 450, 490, and 525 mμ. By combining the glasses

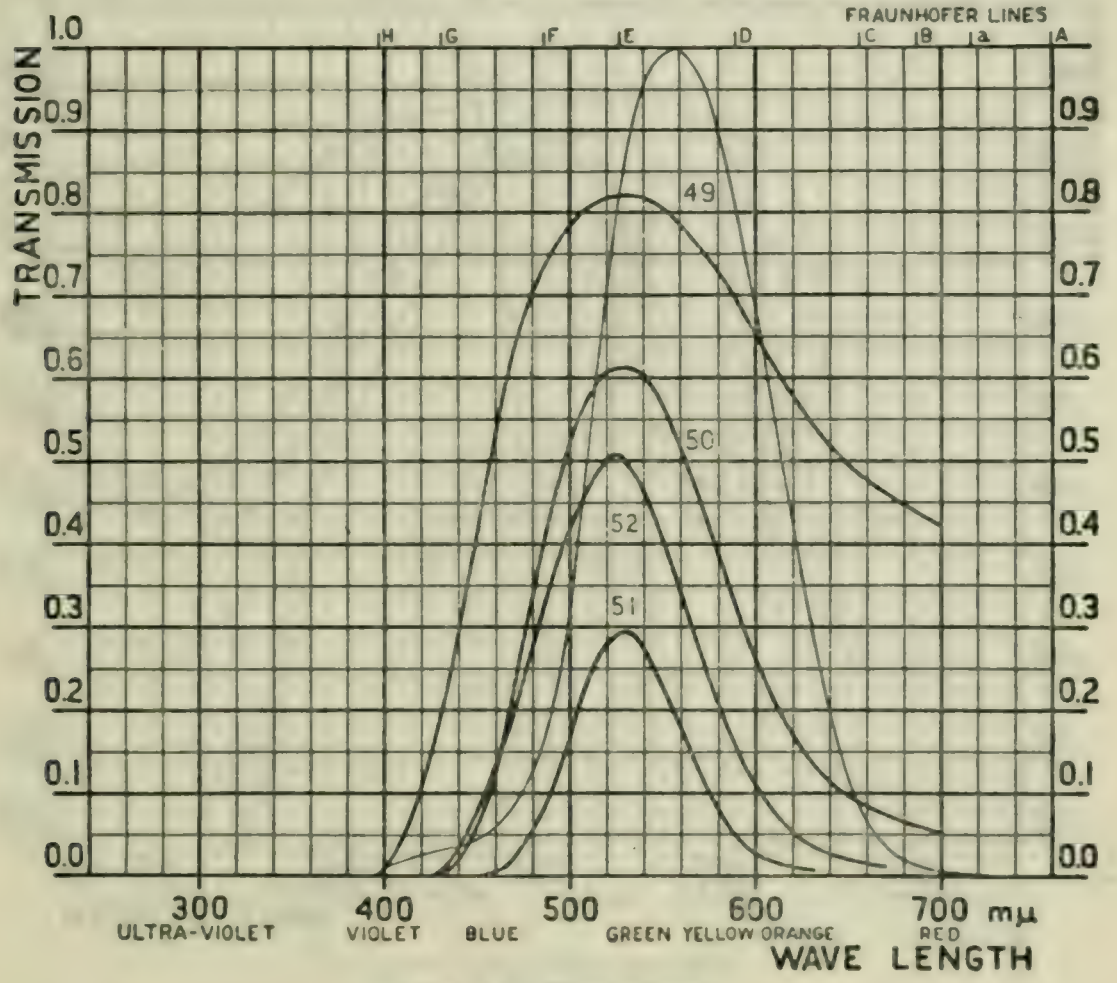


FIG. 12.—*Green glasses*

49="4930," 0.28 mm; 50=same, 1.03 mm; 51=same, 2.99 mm; Jena. 52="Sextant Green," 1.66 mm; C. G. W.

of Figs. 6 and 7 with those of Figs. 12, 13, and 14 and certain of the glasses of Figs. 16 to 19, fairly narrow regions of the spectrum may be isolated, the values of the transmission and wave length at the maximum being more or less controllable. This isolation of narrow regions of the spectrum is of value in various visual and photographic work.

A combination of glasses similar to 25 and 69 gives a low-transmission, dichromatic, red-blue screen which has proved of value in the detection of camouflage.

The combination of glasses 35 and 11 has been proposed[16] as a means of protecting the eyes from the intense radiation from accidental arcs between copper parts in electrical installations, while transmitting sufficient light to permit of its being worn in goggles by the workmen under ordinary illumination. Protection is required not only against the ultra-violet, but also against the

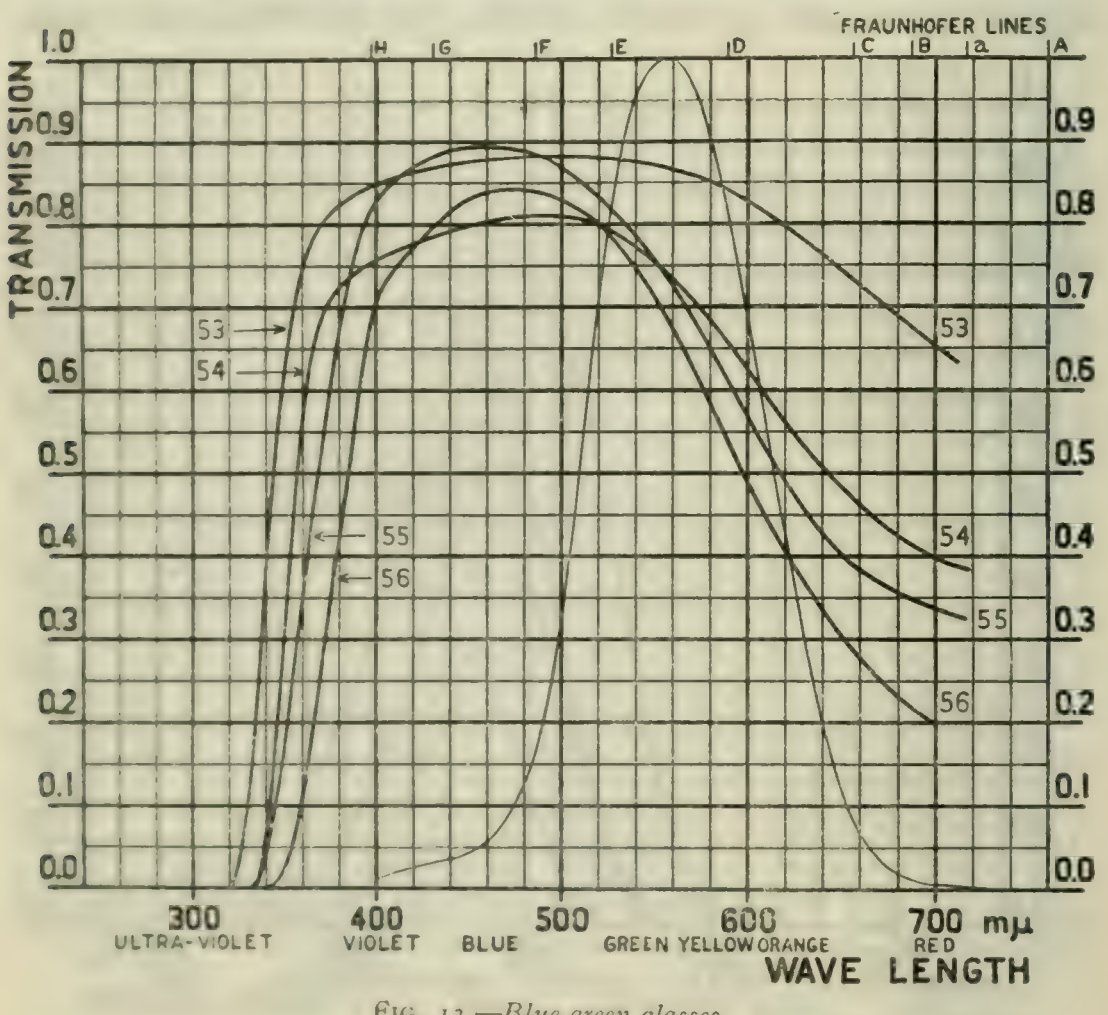


FIG. 13.—*Blue-green glasses*

[illegible] 1.24 mm, 54=same, 3.09 mm; 55="G171IZ," 3.12 mm; 56=same, 4.62 mm; C. G. W.

blinding flash of light from the arc. The principal visible lines in the copper arc are shown in Fig. 22, in which is also plotted the transmission curve for the combination of glasses above mentioned. Most of the light is due to the yellow lines and the many lines below 530 mμ. As may be noted from the figure, these lines are all largely absorbed, as well as those in the ultra-violet, but a considerable amount of daylight or light from any other source having a continuous spectrum is transmitted.

[16] Letter of [illegible] to E. B. Rosa; Mar. 15, 1918. A combination of glasses 31 and 11 would be considerably more efficient than the filter here proposed. Glass 31 was not available at the time this proposal was made.

### 11. MONOCHROMATIC LIGHT FILTERS.

For various kinds of work it is highly important to have available filters which will transmit monochromatic light from the mercury arc or the hydrogen or helium vacuum tube. The filters whose curves are given in Fig. 23 are advised, many of them having been in use for some time at the Bureau. Usually a combination

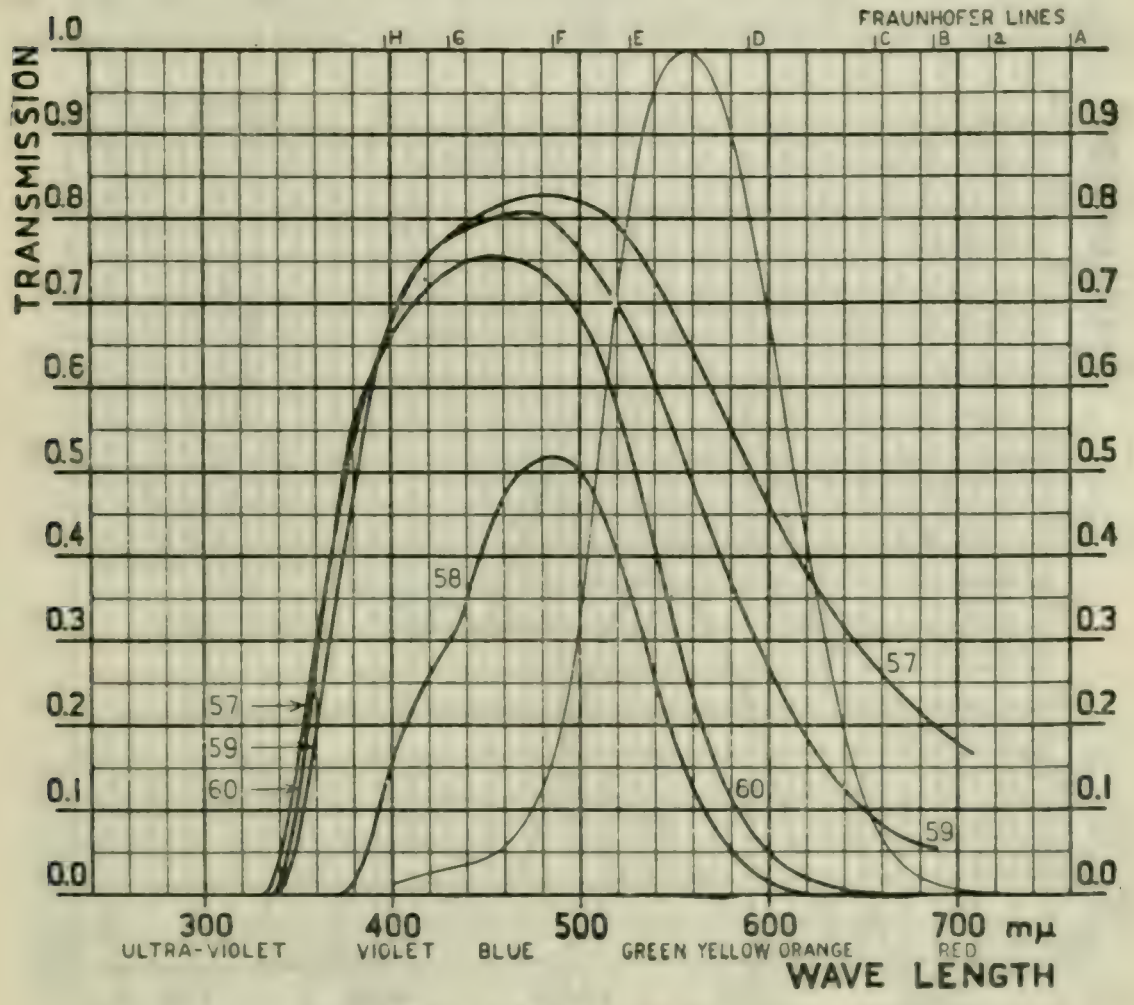


FIG. 14.—*Blue-green glasses*

57= "Green 166[illegible]," 4.92 mm; 58= same, 5.55 mm; 59= "401Z," 2.22 mm; 60= "G584" (old "GT14B"), 4.1 mm; C. G. W.

of glasses is necessary for this purpose, although in some instances a single one is sufficient. In choosing these filters the attempt is made, of course, to obtain as high transmission as possible of the particular line desired, with as high absorption as possible of all remaining lines in the visible spectrum.

In the case of the mercury arc, the filters are so chosen as to absorb even the faint line at 491.6 mμ. The faint red lines are also absorbed by the filters transmitting the blue and violet lines, but they are so faint in comparison with the green and yellow lines that

they need not be absorbed by the filters transmitting these lines. Care must be used in making measurements if the specimen has a strong red or yellow fluorescence.

No trouble is experienced in separating the hydrogen lines. The lines in the extreme violet beginning at 410.2 mμ are absorbed in all cases.

Only the red and yellow lines of the helium spectrum can be efficiently used, as the blue lines are too close together to be

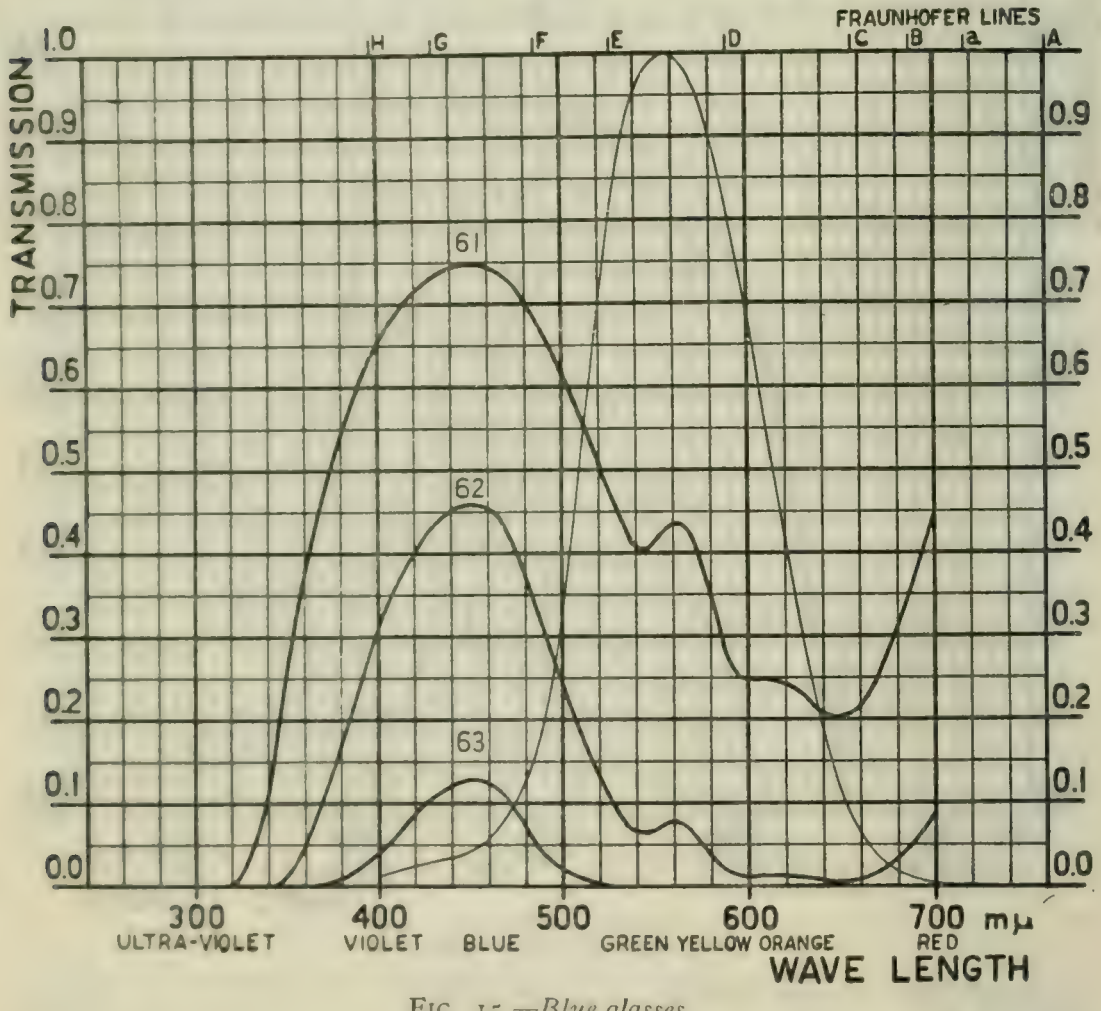


FIG. 15.—*Blue glasses*

61—"[illegible]," 0.41 mm; 62=same, 1.03 mm; 63=same, 2.99 mm; Jena.

separated. The transmission of the far red line at 706.5 mμ by the filter used to transmit the strong line at 667.8 mμ does not introduce error unless the sample being examined transmits the former very highly relative to the latter.

## IV. SUMMARY

1. Spectral transmission curves for 87 samples of glass representing over 50 different kinds, mostly colored, are given in this paper. These curves extend from about 710 mμ throughout the visible

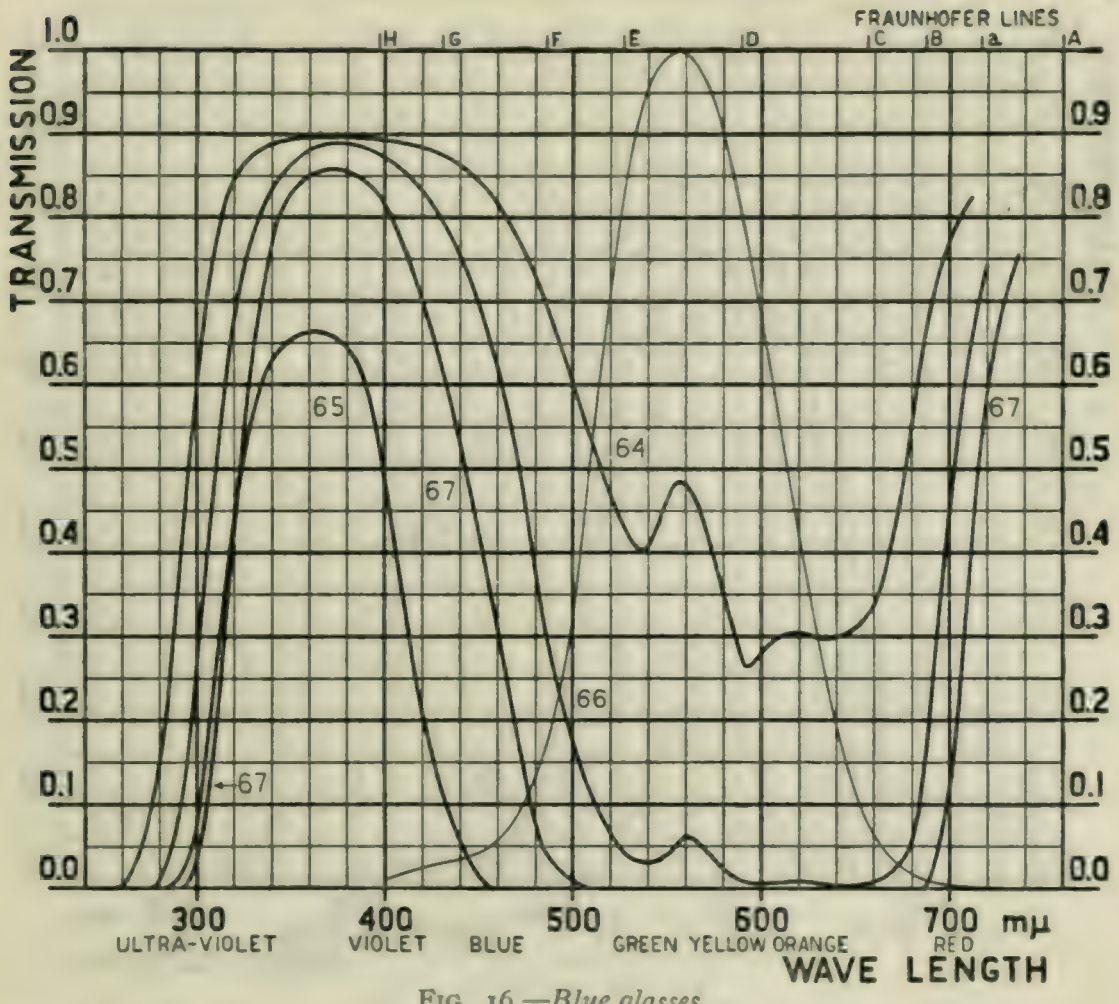


FIG. 16.—*Blue glasses*

64="3653," 0.27 mm; 65=same, 5.45 mm; 66="3654," 1.04 mm; 67=same, 3.00 mm; Jena.

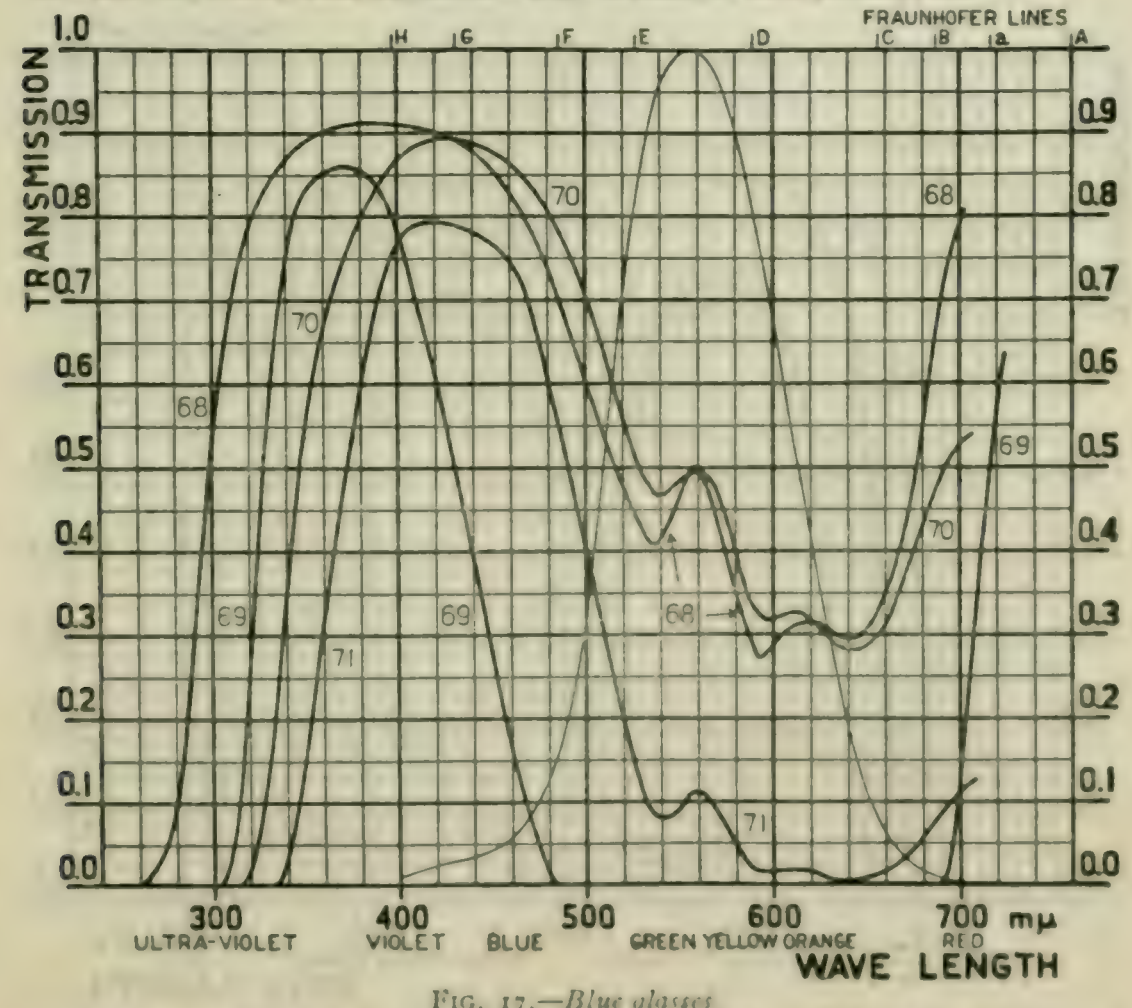


FIG. 17.—*Blue glasses*

68="$G_{5685}$" (old "GT11E"), 0.28 mm; 69=same, 4.02 mm; 70="$G_{5070}$," 0.98 mm; 71=same, 3.39 mm; C. G. W.

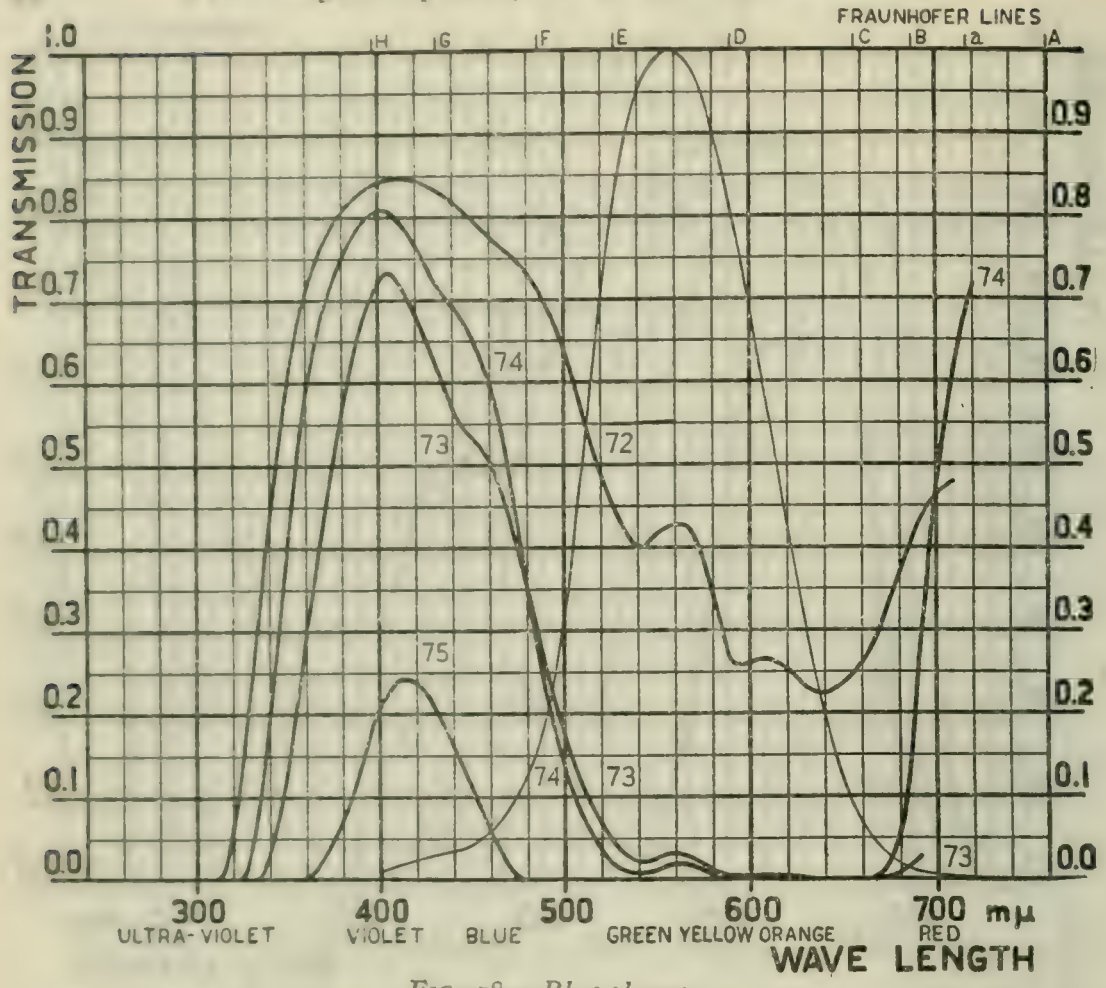


FIG. 18.—*Blue glasses*

73="Blue 100%," 6.92 mm; 74=same, 4.56 mm; 74="Purple 100%," 5.03 mm; 75="$G_{53}$," 2.59 mm; C. G. W.

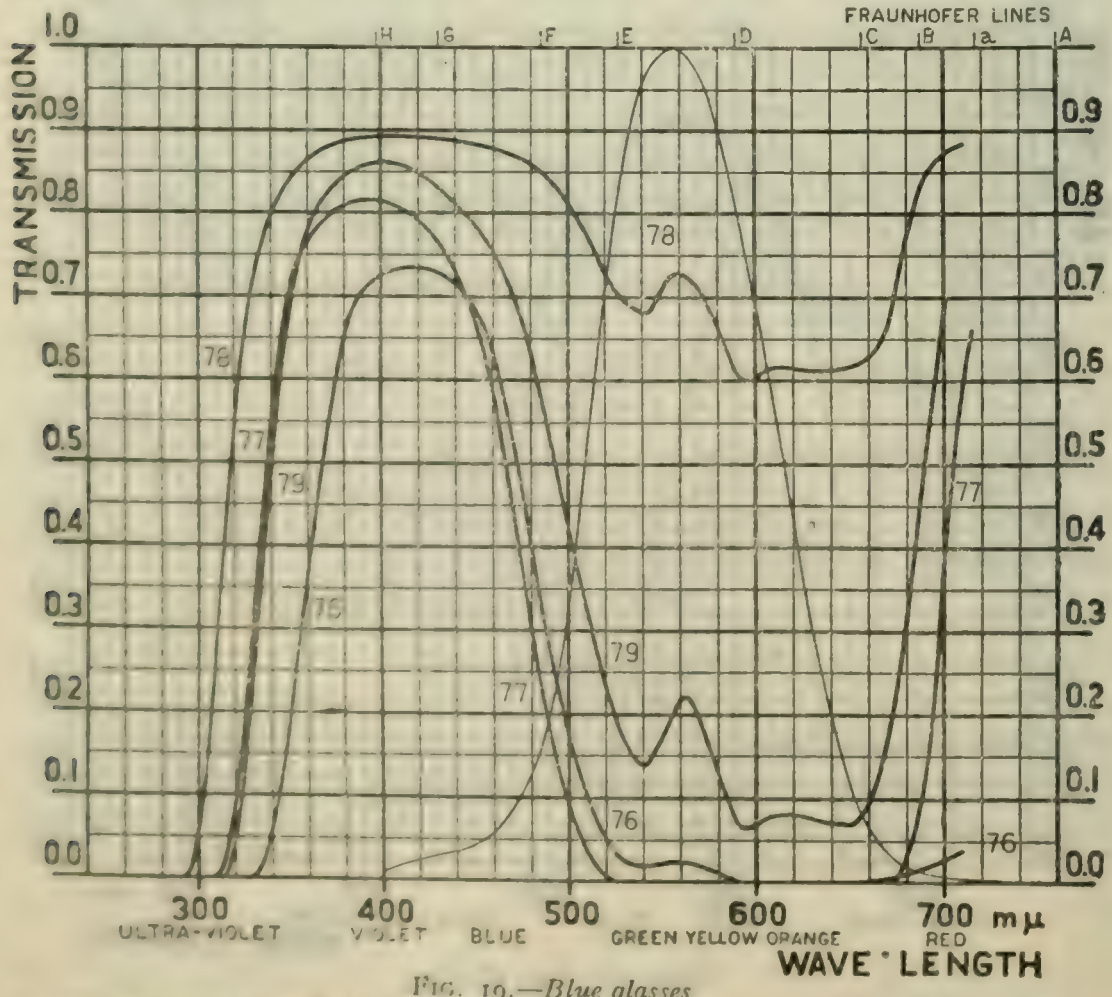


FIG. 19.—*Blue glasses*

76="G₅₃," 2.59 mm; 77="G₅₃A 80%," 2.61 mm; 78="G₅₃D 70%," 2.97 mm; 79=same, 6.22 mm; C. G. W.

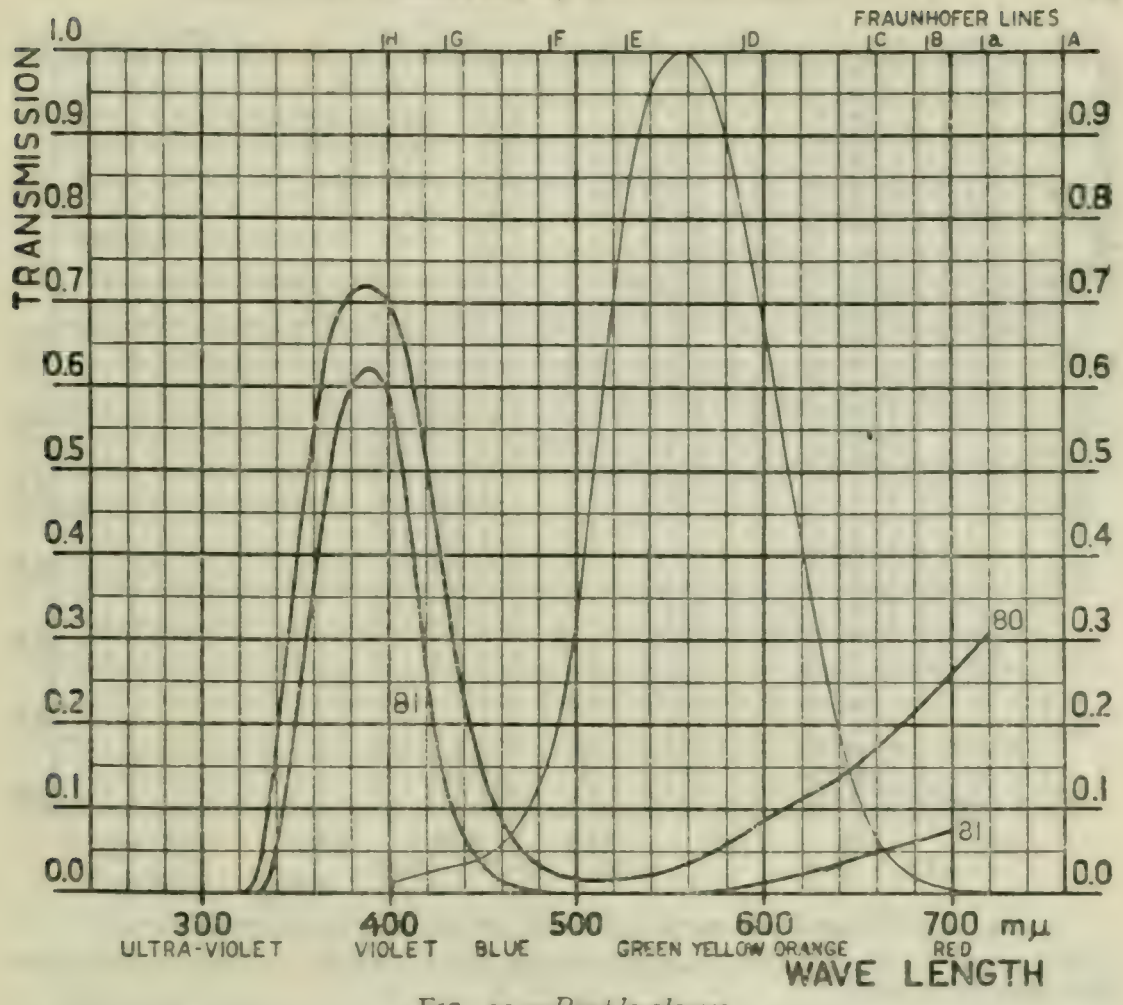


FIG. 20.—*Purple glasses*

80="G172BW5," 5.27 mm; 81="G554 CP," 5.48 mm; C. G. W.

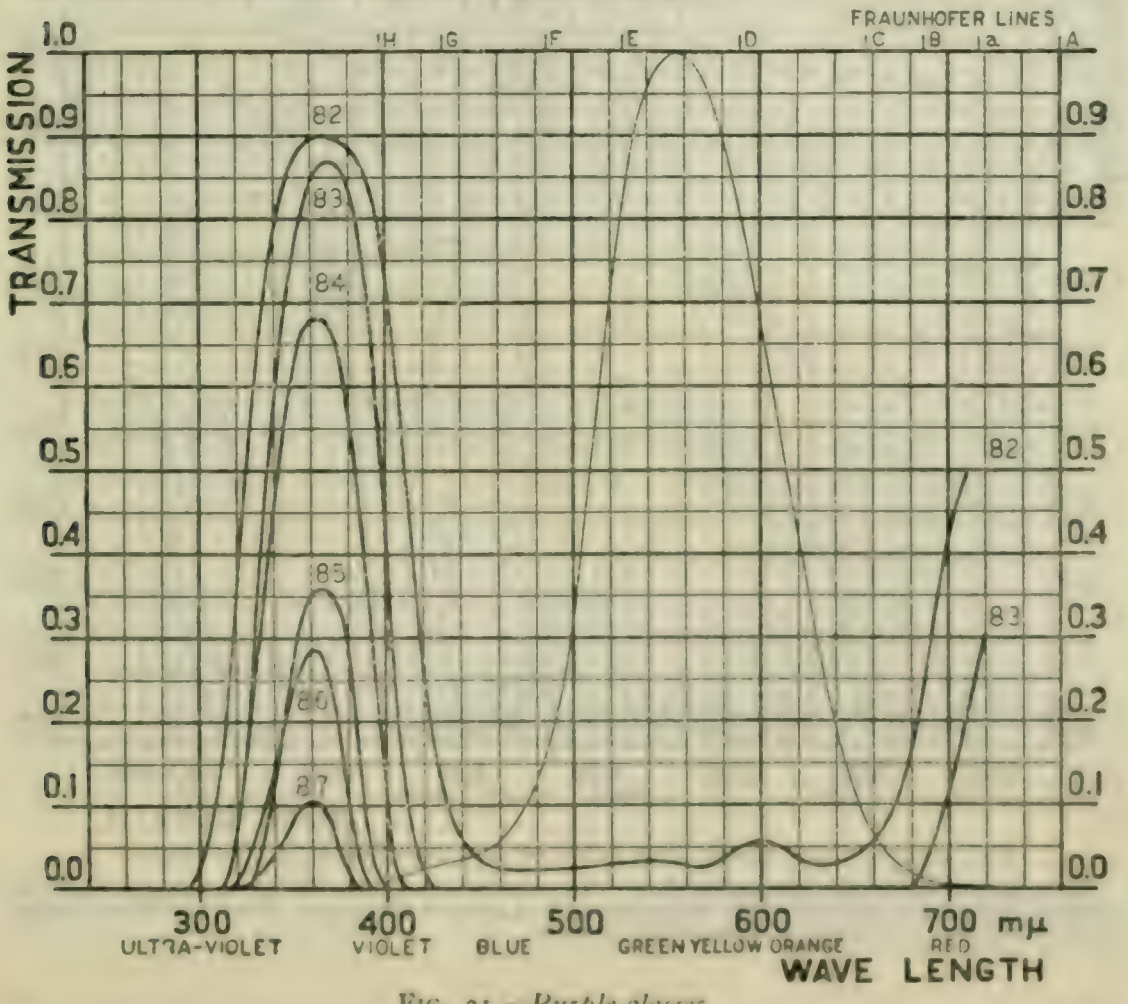


FIG. 21.—*Purple glasses*

82="G586A," (old "G55A62"), 1.03 mm; 83=same, 3.00 mm; 84="G586C," 4.05 mm; 85="G586J," 2.68 mm; 86="G586N," 3.13 mm; 87="G586P," 4.17 mm; C. G. W.

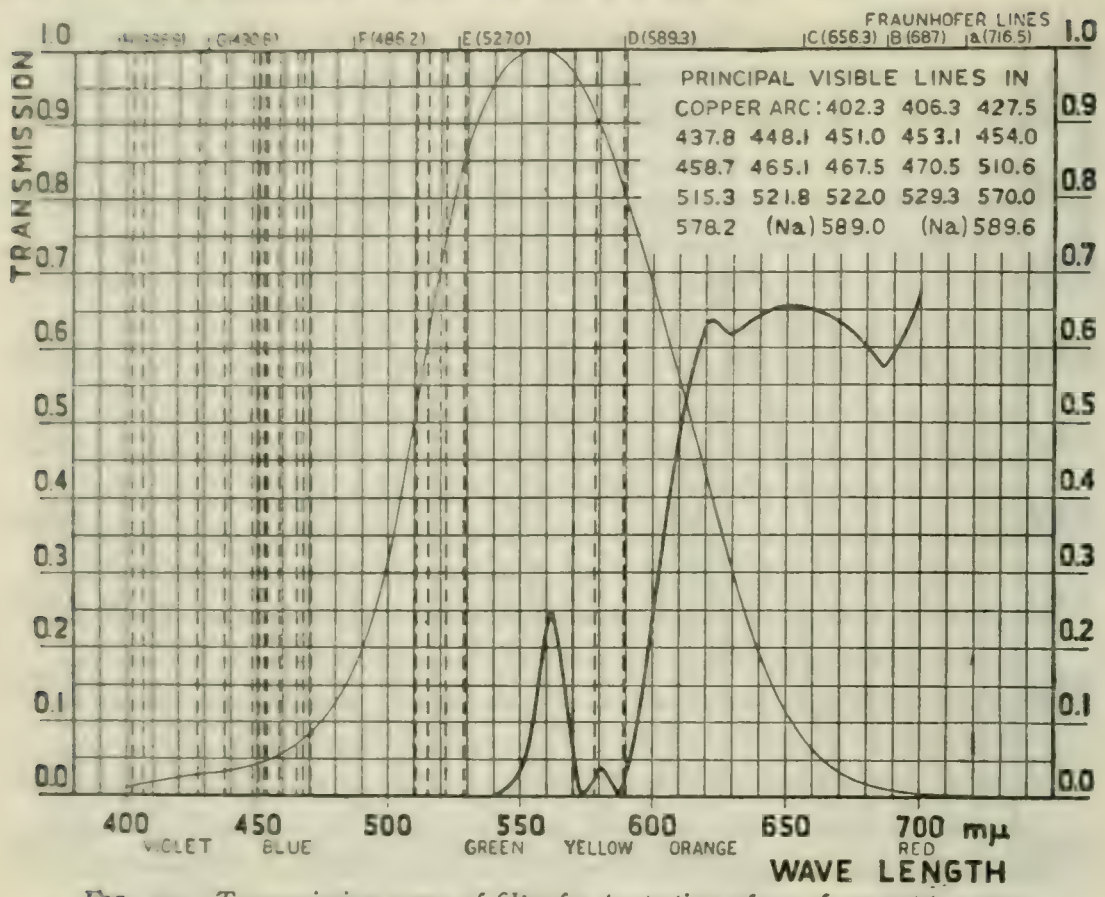


FIG. 22.—*Transmission curve of filter for protection of eyes from copper arcs*

The principal visible spectral lines of the copper arc are given in the figure. The curve is the product of previous curves 11 and 35.

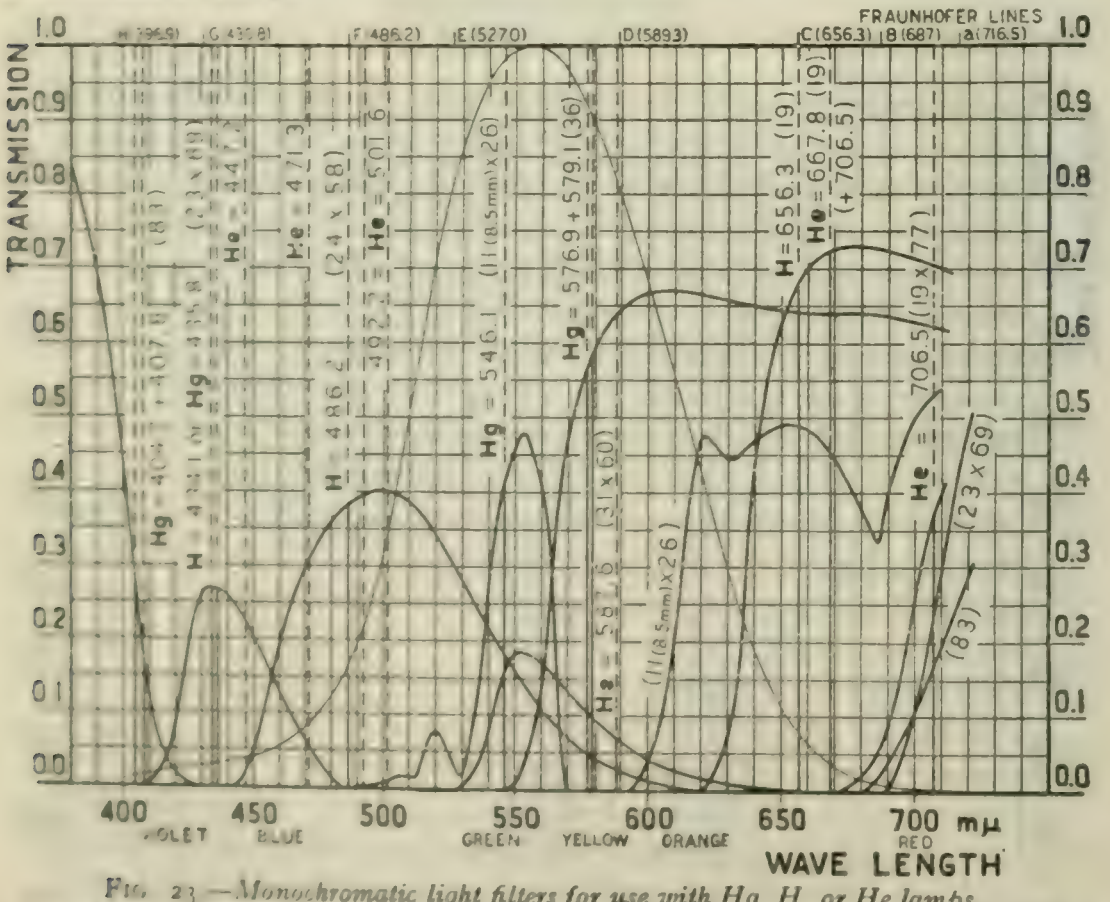


FIG. 23.—*Monochromatic light filters for use with Hg, H, or He lamps*

The principal visible spectral lines are shown. In parentheses are given the curve numbers, from the previous figures, of the glasses used to obtain the curve as given in this figure. The spectral line is made conspicuous by the curve of the filter used to isolate it.

and ultra-violet as far as the specimens have any appreciable transmission.

2. Most of these glasses are of American manufacture, but a comparison is afforded with some samples of Jena glass obtained before the war.

3. Various practical uses to which these glasses may be put are indicated, such as ultra-violet signaling, railway signaling, improvement of visibility both for visual and photographic work, protection of the eyes, and selective ray filters. Of special value is their use as filters to obtain monochromatic light from the mercury, helium, or hydrogen lamps.

WASHINGTON, June 30, 1919.

## APPENDIX

By E. P. T. Tyndall

The source for the ultra-violet spectrophotometer was set up at the Bureau at first as described by Howe.[17] It was soon found, however, that an exceedingly small movement of the electrodes caused the two comparison spectra, taken first and last on the plate, to become unequal. It was almost impossible to get reliable data, as this movement very often occurred during a series of exposures. This trouble was always present in the Cornell set-up, but in less degree than the Bureau apparatus showed. To remedy the difficulty, a trial was made of putting the electrodes perpendicular to the position formerly used; that is, with the spark length parallel to the slit of the spectrograph. The expected ease and permanence of adjustment were realized, and, in addition, another improvement was noted.

This improvement may be seen by examining Figs. 24, 25, and 26. Fig. 24 shows a print from a negative taken with the apparatus at Cornell (horizontal spark). Fig. 25 is one taken at the Bureau on the original set-up. It will be noted that in both cases the two spectra, for any exposure, are only in contact in the middle region of the spectrum. In the extreme ultra-violet and in the visible region there is considerable spread, enhancing the difficulty of making photometric observations for a considerable range. Fig. 26 is a print from a negative taken with the spark length parallel to the slit (vertical spark). The spectra here make contact throughout their whole length, and the ease and accuracy of determining points of equal density are greatly increased.

Several other minor changes have been made. Brass rods about 1.2 mm in diameter have been substituted for the aluminum ones used by Howe, as the former do not disintegrate so fast under the mechanical shock of the spark. The gap under water is generally about 1.5 cm, so that there are no lines superposed on the continuous spectrum. This necessitates the photographing of a known spectrum (aluminum spark in air) at least twice on each plate. The spark is placed directly in front of the slit and can be swung out of the way while not in use.

[17] Loc. cit.

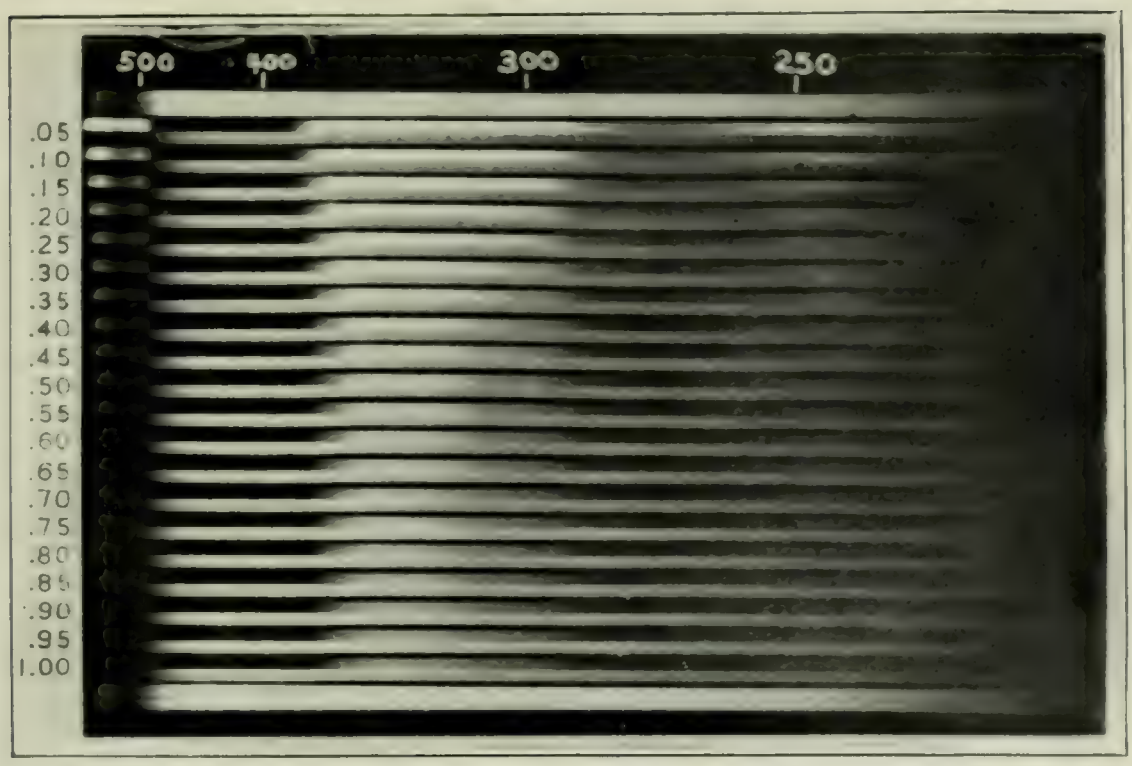


FIG. 24.—*Paranitrosodimethylaniline, 0.000034 g per cubic centimeter of distilled water, 1 cm layer, February 24, 1917, K. S. G. at Cornell University*

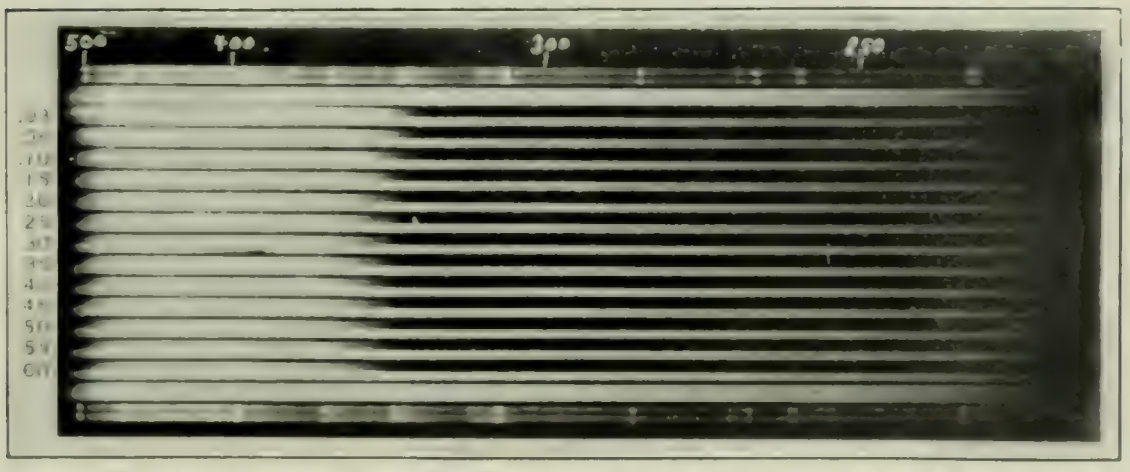

FIG. 25.—*Corning "Blue 100%" (curve 73, Fig. 18), August 17, 1918, E. P. T. T. at Bureau of Standards*

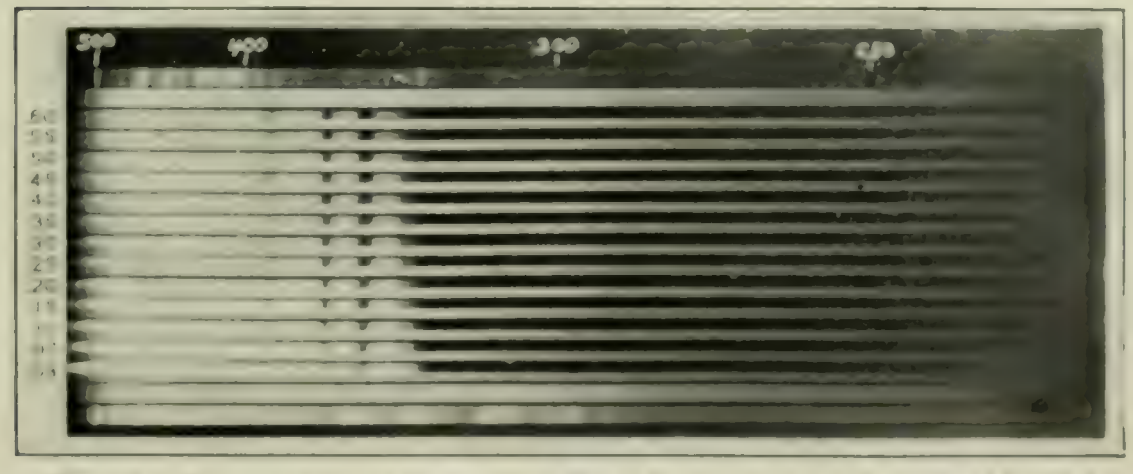

FIG. 26.—*Holmium nitrate (impure), 0.282 g of nitrate to 1 g of solution (distilled water), 1 cm layer, December 20, 1918, E. P. T. T. at Bureau of Standards*

Electrode holders have been made which are quite independent of any movements of the distilled-water jar. By means of scales and verniers the vertical and horizontal positions of the two electrodes may be read to 0.1 mm. This facilitates adjustments when they are necessary, though, except for an occasional shortening of the gap, readjustments need seldom be made during the whole life of a pair of electrodes.

Howe's method has up to the present been used in obtaining the transmission curves from the negatives. In most cases, however, the plates have been "spotted" on the glass side several times and corresponding readings averaged. This is a slow process, and to save time and to increase the accuracy of locating the points of equal density a comparator has just been completed. In this comparator the negative is placed over a sheet of milk glass in a brass frame. This frame moves from left to right on roller bearings in a second frame, which moves to and from the observer. The first motion permits of any pair of spectra being moved parallel to their length under a fixed bilateral slit until the point of equality is reached. The position is read by means of a scale on the second frame and vernier on the first. Reference to a calibration curve or table gives the wave length or frequency for the point of match for that particular setting of the sector. The motion of the second frame then allows another pair of spectra to be brought into view. The slit is made adjustable in width, as it is necessary to increase the slit width when the density gradient of the spectrum transmitted through the absorbing substance is gradual. A simple convex lens ($f = 30$ mm) is used to view the slit. All of the above is mounted on a metal box containing an incandescent lamp placed directly below the slit.

WASHINGTON, June 30, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 149

## ESTIMATION OF NITRATES AND NITRITES IN BATTERY ACID

BY

L. B. SEFTON, Assistant Chemist
*Bureau of Standards*

ISSUED FEBRUARY 24, 1920

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## DETERMINATION OF VOLATILES AND MOISTURE IN BATTERY ACID

BY

JOSEPH W. RICHARDS, Ph. D.
Chief, Section of Metallurgy

ISSUED JUNE 15, 1920

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# ESTIMATION OF NITRATES AND NITRITES IN BATTERY ACID

By L. B. Sefton

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| 1. Occasion for the investigation | 3 |
| 2. Scope of the work | 4 |
| II. Methods for the determination of nitrates | 5 |
| 1. Diphenylamine method | 5 |
| 2. "Hydrostrychnique" method | 5 |
| 3. Brucine method | 6 |
| III. Methods for the determination of nitrites | 8 |
| 1. Iodide method | 8 |
| 2. Indol method | 8 |
| 3. Dimethylaniline method | 9 |
| IV. Conclusions | 9 |


## I. INTRODUCTION

### 1. OCCASION FOR THE INVESTIGATION

In connection with the testing of sulphuric acid to be used in storage batteries, it became apparent that the methods commonly used for the detection and estimation of small amounts of nitrates and nitrites in sulphuric acid differed not only in sensitiveness, but also in reliability. Since the usual specifications for battery acid do not allow more than a few thousandths of 1 per cent of nitrogen in any form, a high accuracy is required of the method used for its estimation. The determination of nitrogen as ammonia presented no difficulties. Many papers have been written about methods for the determination of small amounts of nitrates and nitrites in water, and a few of them can be used in a medium of sulphuric acid, but no comparison seems to have been made of methods directly applicable to battery acid.

This Bureau through the kindness of a number of manufacturers has obtained considerable information about the methods in commercial use at the present time. These methods differ

widely. For the most part they are qualitative methods by which an experienced operator may quickly decide whether or not the material is suitable for batteries. An increasing realization of the importance of the purity of battery acid makes quantitative methods desirable.

## 2. SCOPE OF THE WORK

Practical reasons render it necessary that the methods selected should combine reliability, accuracy, and sensitiveness with speed and simplicity. Elaborate apparatus and costly reagents are to be avoided as well as any preliminary treatment of the samples by evaporation or neutralization which tend to produce loss or contamination. It is also important that the reagents selected should not be affected by the other impurities likely to be present in battery acid. These restrictions make colorimetric methods alone applicable. A comparative study was made of methods used for the detection of nitrates and nitrites in sulphuric acid. The result of that study is embodied in this paper whose purpose is (1) to point out the methods proven to be most reliable and (2) to suggest the best conditions for using them.

One of the main facts brought out by the various experiments was that nitrates, as such, could not be estimated in the presence of nitrites, if the battery acid, either fresh or used, had been made up for more than three days. In view of that fact the methods selected for nitrates are those which will give the same results with nitrites under conditions above stated, so that the final results of analysis may be expressed in terms of nitrates and nitrites. The use of urea and hydrazine sulphate which has been suggested [1] to prevent the interference by nitrites of nitrate determinations was not satisfactory. Urea did not entirely prevent the interference and hydrazine sulphate prevented the formation of characteristic colors with nitrates as well as with nitrites.

For some reason not yet determined fresh battery acid and acid which had been used in batteries showed under the same given set of conditions appreciable differences in the depths of color given by the various reagents studied. These differences varied in amount and direction with the reagents, but were great enough in every case to make it necessary that the standards be made up

[1] Niemczycki, Arch. Chem. Mikros, 4, p. 125 (C. A., 5, p. 2475; 1911). Sen and Dey, Z. anorg. Chem., 74, p. 50, 1912.

with used electrolyte (nitrate and nitrite free) when the sample of acid under examination has been used in a battery.

According to the specifications in current use, the impurities most often mentioned are nitrates, nitrites, ammonia, arsenic, chlorides, copper, and iron. Standard solutions of these substances were made up in a sulphuric-acid solution of specific gravity 1.28 and used in all experiments described in this paper.

## II. METHODS FOR THE DETERMINATION OF NITRATES

### 1. DIPHENYLAMINE METHOD [2]

Although the unreliability of this method has been pointed out by Caron [2] and others, it is desired to emphasize that unreliability in this paper, because of the common use of the method in the commercial testing of battery acid. Tests showed that the characteristic blue color given by the reagent with nitrates was given also by nitrites, iron, and arsenates, and by sulphuric acid itself, to such an extent as to render the method useless.

### 2. "HYDROSTRYCHNIQUE" METHOD

This method, first suggested by Deniges,[3] has been found to be satisfactory if used as follows: Prepare the reagent by dissolving 1 g of strychnine sulphate in 100 cc of water. Immediately before using, mix 5 cc of this solution with 5 cc of concentrated hydrochloric acid, and reduce by allowing to stand for 10 minutes with 4–5 g amalgamated zinc. Use the resultant "hydrostrychnique solution" for the tests.

To 10 cc of the battery acid (specific gravity about 1.28) to be tested, add 0.5 cc of the hydrostrychnique solution and mix well. Add 10 cc concentrated sulphuric acid (specific gravity 1.83) and mix. If nitrates or nitrites are present, a vivid pink color, permanent for several hours, will develop. Compare at the end of five minutes with nitrate standards similarly and simultaneously treated.

The reagent was found to be unaffected by solutions containing 0.005–0.010 per cent of ammonia, arsenic, copper, and chlorides. A solution containing 0.005 per cent of iron gave an orange color. If iron is present in a nitrate or nitrite sample, this orange color so changes the hue of the characteristic pink color as to render the method useless for the quantitative determination of nitrates and

[2] Caron, Annal. Chim., anal., 16, p. 211; 1911.
[3] Deniges, Bull. Soc. Chim., 9, p. 544; Annal. Chim. anal., 19, p. 221; 1914.

nitrites. Nitrites, as has been implied, give with the reagent in solutions of acid which have been made up for more than three days a pink color practically identical in hue and depth with that given by equivalent amounts of nitrates. The method is sensitive under the conditions given to one part per 5 000 000 with fresh acid. Since the color that it gives is much more stable than that given by brucine, its use is recommended when the acid under examination contains no iron and when iron-free zinc can be obtained.

### 3. BRUCINE METHOD [4]

This method is in use in the commercial testing of battery acid and gives good results when the conditions stated below are rigidly adhered to both in samples and standards.

The reagent is prepared by dissolving 0.2 g brucine in 100 cc of pure concentrated sulphuric acid. It must be made up fresh each time it is used. The solution has a faint yellow color.

To a 10 cc sample of the battery acid to be tested add double its volume of pure concentrated sulphuric acid and cool to room temperature (about 25° C). Add 2 cc of the reagent and mix quickly and thoroughly. If nitrates or nitrites are present a rose-red color will develop; this changes quickly to a sulphur yellow and then more slowly to a golden yellow. When the sulphur yellow appears, compare with standards similarly and simultaneously treated. The sulphur-yellow color is chosen as the end point, because the rose-red color changes too rapidly to permit of a satisfactory comparison with the standard and the golden-yellow color is not sensitive enough to different amounts of nitrates or nitrites. The chief disadvantage of the method is the number and varying rates of these color changes.

Effect of Impurities.—The brucine test was unaffected by the presence of 0.005 to 0.025 per cent of iron, arsenates, arsenites, chlorides, copper, and ammonia. In solutions of acid density below 1.70, nitrites affect it to the same extent as nitrates. Nitrites in solutions of 1.83 specific gravity have no effect upon it.

Effect of Acid Density.—Since preliminary tests showed that the production and changes of color with the brucine reagent were accelerated by increasing acid density, it was desirable to select a density at which the development of colors would occur within a convenient length of time. To determine this, a series of tests was made on samples whose volumes, temperatures, and

[4] Lunge and Lwoff, Zeit. angew. Chem., 7, p. 345; 1894. Analyst., 38, p. 450; 1913.

nitrate concentrations were identical, but whose acid densities varied from 1.835 to 1.605. The time required for the development of the sulphur-yellow color varied from one-half minute in the first to one hour in the last. In the samples in which the density was greater than 1.735 the change from sulphur to golden yellow was so rapid as to make comparison with standards difficult. In samples in which the acid density was below 1.635, the change was so slow as to make comparisons unreliable. The best acid density was found to be between 1.65 and 1.70.

Effect of Nitrate Concentration.—A set of experiments was made on samples whose temperature, sulphuric-acid concentration, and absolute nitrate content were the same, but whose nitrate concentration, i. e., whose volumes varied. The colors developed very much more rapidly in the samples whose nitrate concentrations were high. This fact tends to decrease the value of the method as a quantitative one.

Effect of Temperature.—An increase in temperature produces with this method an increase in the speed of color production and change. A sample at 23° C showed a sulphur-yellow color in about two minutes, while a similar sample at 70° C gave the same color within 10 seconds.

Effect of the Age of the Reagent.—A very great difference was observed among samples treated under similar conditions with brucine solutions which had been made up for varying lengths of time. With a reagent made up for less than 15 minutes, one part of nitrate in 5 000 000 was easily detected; but with a solution made up for a couple of hours not more than one part nitrate in 2 000 000 could be detected, and with solutions made up for several days, only one part in 500 000.

Sensitiveness.—In fresh electrolyte, the method is accurate to one part of nitrates or nitrites in 5 000 000; in used electrolyte, to one part in 400 000.

Modification of the Brucine Method.—The indifference of brucine to iron makes it so valuable as a reagent that efforts were made to render it more sensitive with used acid. The net results of these efforts is a reagent prepared in much the same way as the "hydrostrychnique" reagent. One g of the brucine was dissolved in 2 cc concentrated sulphuric acid and that solution mixed with 50 cc water immediately before using; 5 cc of this solution mixed with 10 drops of concentrated sulphuric acid were allowed to stand in contact with 4 or 5 g of amalga-

mated zinc for 5 or 10 minutes; 2 cc of the resultant solution was used for each test.

The preliminary tests showed that this modified reagent was much more sensitive to nitrates and nitrites in used acid than the original brucine reagent. Unfortunately, however, it is affected by iron, though not to so great an extent as the "hydrostrychnique" reagent. The only advantage that it possesses over the latter reagent is the fact that it does not give any color with impurities other than iron.

## III. METHODS FOR THE DETERMINATION OF NITRITES

Nitrites are oxidized to nitrates in dilute sulphuric acid,[5] and it was further found that the rate of oxidation increased with the dilution of the acid. Experiments made on four solutions of equal initial nitrite concentration, but in acid of densities varying from 1.835 to 1.28 showed that the nitrites in the solution of 1.835 density had suffered no change after 10 days while that in the solution of 1.28 density was practically all changed to nitrates at the end of three days. Battery acid which has been made up for more than three days then is not likely to contain any nitrites, but since the methods in this paper are designed for the examination of any acid intended for battery purposes, three methods selected from a large number as those most likely to fulfill the requirements were studied.

### 1. IODIDE METHOD [6]

It is desired to emphasize the unreliability of this method which although generally known to be unreliable in the presence of oxidizing agents—even in the presence of atmospheric oxygen[7]—continues to be used to some extent in the commercial testing of sulphuric acid. The modifications proposed[7] are not practicable with battery acid.

### 2. INDOL METHOD [8]

This method was found to be a good qualitative one if used as follows: Prepare the reagent by dissolving 0.02 g of indol in 75 cc of 95 per cent ethyl alcohol. To 10 cc of the battery acid to be tested in a Nessler tube add 10 cc of concentrated sulphuric acid and 3 cc of the reagent and mix. If nitrites are present a

[5] Lunge, Zeit. Angew. Chem., 15, p. 1; 1901.
[6] Blanc, Annal. de Chim. Anal., 17, p. 216; 1912.
[7] Dienert, Annal. Chim. Anal., 1, p. 4; 1919.
[8] M. Dane, Bull. Soc. Chim., 9, p. 354; 1911.

permanent pink color appears. Unfortunately, however, a yellow color is also produced when only 0.001 to 0.002 per cent of ammonia, arsenates, arsenites, iron, chlorides, or copper are present. Although this yellow color affects the pink color to such a degree as to render the method useless for quantitative purposes, the interference is not so serious as to disqualify the method as a qualitative test for nitrites. The characteristic pink color was not affected by variations in acid density from 1.28 to 1.70, while above 1.70 the color tends toward yellow. When the nitrite content is below 0.001 per cent, and the acid density is above 1.35, the colors tend toward yellow. An acid density of 1.28 to 1.35 is recommended.

### 3. DIMETHYLANILINE METHOD [9]

This method was found to be the most satisfactory one for the detection of nitrites if used as follows: The reagent is prepared by dissolving 2 g of dimethylaniline in 3 cc concentrated hydrochloric acid and 25 cc of water. Three drops of the reagent are added to 25 or 30 cc of the battery acid to be tested and allowed to stand for 10 to 30 minutes. If nitrites are present, a yellow color appears. Compare with standards similarly and simultaneously treated. The test is unaffected by the presence of 0.005 to 0.010 per cent of any other impurities.

Unlike the indol, this method gives slightly but uniformly deeper colors with the fresh electrolyte than with the used electrolyte. Time is an important factor in the development of the color in very weak solutions of nitrite. The yellow color sometimes does not appear for 30 minutes. The gradation in color with varying amounts of nitrites is marked and thus renders it an excellent quantitative reagent. It will detect nitrites in amounts as low as one part in 1 000 000 (0.0001 per cent). In acid which has been used in a battery it will detect one part in 250 000 (0.0004 per cent).

## IV. CONCLUSIONS

1. The methods recommended in this paper have been selected from more than 50 methods mentioned in literature, as being the most suitable and reliable for battery purposes.

2. The methods recommended do not involve a complicated procedure or require elaborate apparatus. They are therefore available for quantitative determinations in an ordinary laboratory.

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[9] E. Holl Miller, Analyst, 37, p. 345; 1912.

3. Nitrates can not be estimated in the presence of nitrites, while nitrites can be estimated in the presence of nitrates.

4. The results from the "hydrostrychnique" and from the brucine methods may be expressed in terms of the total quantity of nitrates and nitrites.

5. The diphenylamine test for nitrates and the iodide test for nitrites are unreliable.

6. In the absence of iron, the "hydrostrychnique" or the modified brucine test is recommended for the determination of nitrates and nitrites.

7. In the presence of iron, only the original brucine test may be used for the determination of nitrates and nitrites.

8. The dimethylaniline test was found to be best for the determination of nitrites.

WASHINGTON, August 20, 1919.

DEPARTMENT OF COMMERCE

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## PHYSICAL TESTS OF MOTOR-TRUCK WHEELS

BY

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*Bureau of Standards*

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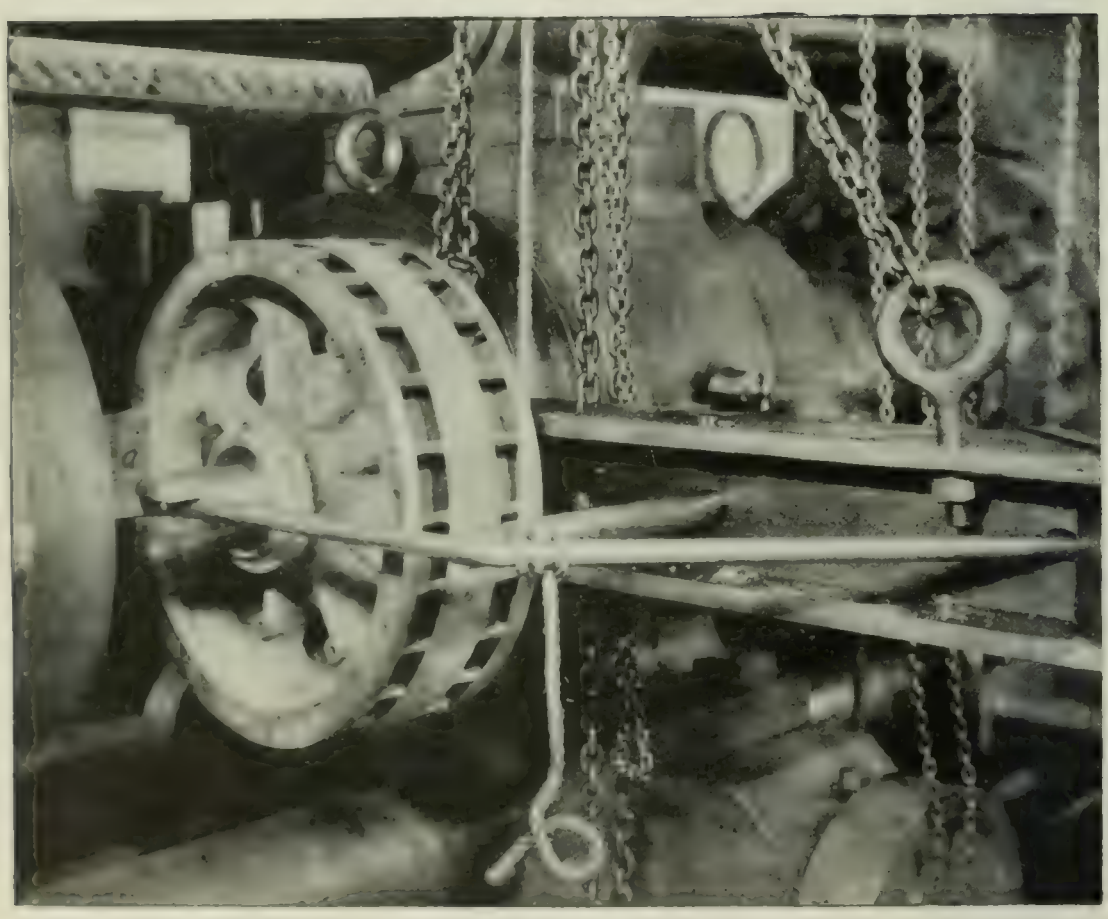

FIG. 3.—*Side-thrust test*

# PHYSICAL TESTS OF MOTOR-TRUCK WHEELS

By Charles P. Hoffmann

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Wheel requirements | 4 |
| III. List of wheels tested | 5 |
| IV. Preparation of the wheels for test | 5 |
| V. Radial-compression test | 6 |
| VI. Side-thrust test | 10 |
| VII. Distribution of stress in wheel | 13 |
| 1. Stresses in rim of wheel | 16 |
| 2. Stresses in hub of wheel | 18 |
| 3. Stresses in spokes of wheel | 18 |
| VIII. Conclusions | 18 |
| IX. Summary sheets and curves | 19 |


## I. INTRODUCTION

In designing Class B military trucks, it was found desirable to develop a metal wheel having the good qualities of all the wheels on the market. No comparative values were available, however, and there was no time for service tests. The Bureau of Standards was therefore called on to make laboratory tests.

Cast steel, pressed steel, wrought iron, and wooden wheels were submitted by motor-truck wheel manufacturers and subjected to radial compression and side thrust or skid tests.

In the meantime the representatives of the companies interested, in cooperation with the Quartermaster's Department of the United States Army, designed a cast-steel wheel which they called the "Composite wheel."

Samples of these wheels were cast and were sent to the Bureau of Standards where they were tested in the same way as the other wheels. Certain alterations in design were found to be desirable. These were made and new wheels cast which were in turn tested. They proved to be satisfactory and were accepted by the Quartermaster's Department.

## II. WHEEL REQUIREMENTS

The requirements listed below were considered essential in a wheel, and the tests were so conducted that information concerning these requirements might be obtained.

(*a*) Each wheel should be strong enough to support its proportionate share of the weight of the truck and of the maximum load which the truck is designed to carry.

(*b*) Each wheel should be strong enough to resist suddenly applied loads and resilient enough to absorb a large part of the shock.

(*c*) The circumference of the wheel should remain approximately circular.

(*d*) The wheel should be capable of sustaining stresses due to side thrust. These may be introduced by skidding, by turning, or by running on roadways which are crowned or have a side slope.

There should be no joints or bolts that will be loosened by radial compression, side thrust, vibration, shock, or climatic conditions.

The weight of the wheel should be as low as possible without reducing the strength of the wheel below that of the rest of the truck.

## III. LIST OF WHEELS TESTED

The following wheels were submitted for test:

TABLE 1

[Unless otherwise noted the wheels were tested without tires, bearings, or brake bands. The weights listed are the weights of the wheels as tested. The dimensions given in the description are the dimensions of the wheel fitted with a tire]

| Wheel No. | Description | Weight in pounds | Wheel No. | Description | Weight in pounds |
|---|---|---|---|---|---|
| 1 | Rear wheel, 36 by 10 inches; wooden wheel; 14 spokes | 252 | 13 | Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; box rim | 286 |
| 2 | Front wheel, 36 by 5 inches; cast-steel disk; box rim | 169 | 14 | Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; composite design | 132 |
| 3 | Rear wheel, 36 by 10 inches; cast-steel disk; box rim | 268 | 15 | Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; composite design | 249 |
| a4 | Front wheel, 40 by 6 inches; pressed-steel corrugated web; channel iron rim | 181 | 16 | Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; composite design | 120 |
| a5 | Rear wheel, 40 by 12 inches; pressed-steel corrugated web; channel iron rim | 354 | 17 | Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; composite design | 273 |
| a6 | Rear wheel, 36 by 6 inches; cast steel; 8 +spokes; brake band cast on wheel | 215 | 18 | Rear wheel, 40 by 10 inches; cast steel; 7 hollow spokes; composite design | 325 |
| 7 | Front wheel, 36 by 5 inches; cast steel; 8 U spokes; box rim | 134 | 19 | Rear wheel, 40 by 12 inches; cast steel; 7 hollow spokes; composite design | 325 |
| 8 | Rear wheel, 36 by 10 inches; cast steel; 8 U spokes; box rim | 274 | 20 | Front wheel, 36 by 5 inches; malleable iron; 7 hollow spokes; composite design | 141 |
| 9 | Front wheel, 36 by 5 inches; cast steel; 7 U spokes; box rim | 136 | 21 | Rear wheel, 40 by 10 inches; malleable iron; 7 hollow spokes; composite design | 288 |
| 10 | Rear wheel, 36 by 10 inches; cast steel; 7 U spokes; box rim | 321 | | | |
| 11 | Front wheel, 36 by 5 inches; cast steel; 5 hollow spokes; box rim | 144 | | | |
| 12 | Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; box rim | 130 | | | |

a Submitted by Ordnance Department, U. S. Army.

## IV. PREPARATION OF THE WHEELS FOR TEST

The wheels submitted were all without tires and in most cases were without bearings or brake bands. Where brake bands were attached they formed an integral part of the wheel and were not removed before the wheel was tested. All bearings were removed and brass bushings substituted. The contact area between the brass bushing and the hub was made equal to that between the bearing and the hub.

All wheels were fitted with these brass bushings to make possible the use of a 4-inch axle for the rear wheels and a 3½-inch axle for the front wheels.

Holes were drilled at four points, 90° apart on the edge of the rim of each wheel, so that dial gages, used for measuring the deformation of the wheel under radial stress, could be fastened to the wheel.

TESTING MACHINE USED.—The Bureau of Standards Emery hydraulic testing machine, having a capacity of 2 300 000 pounds, was used for both the radial-compression and the side-thrust tests.

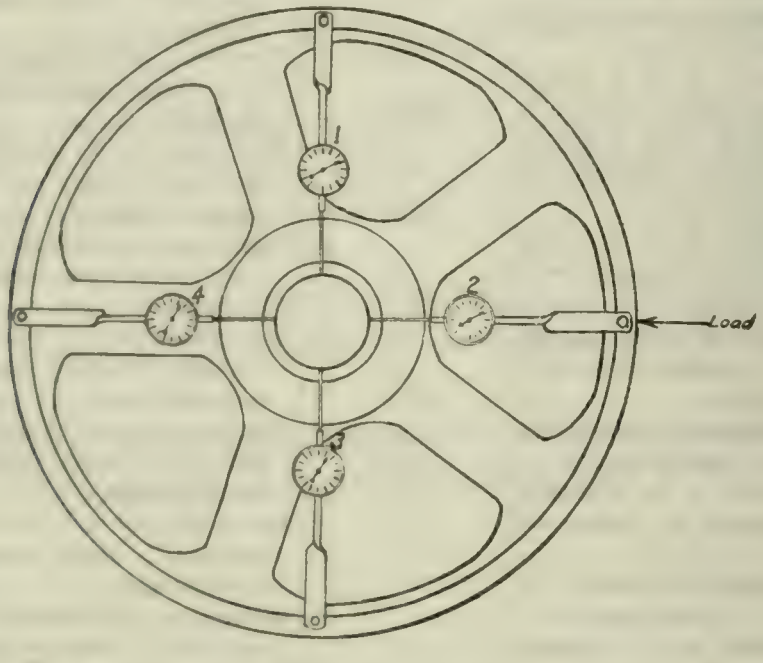


FIG. 2.—*Location of dial gages for radial-compression tests*

## V. RADIAL-COMPRESSION TEST

For the radial-compression test the wheel was placed on a short axle (*a*) as shown in Fig. 1. This axle was supported on both sides of the wheel by bearing blocks (*b*).

Load was then applied through a block at the rim. This block distributed the load over the full width of the rim and along an arc of 6 inches. The wheel was placed so that the load was applied to a section of the rim between spokes.

The deformation of the wheel under load was measured at points 1, 2, 3, and 4. These points were on the edge of the rim of the wheel and 90° apart, No. 2 being at the point of application of load. Ames dials were adjusted as shown in Fig. 2, and the deformations measured between the axle and the rim of the wheel.

These measurements were made at various loads as the load was increased from 1000 pounds to the maximum load recorded

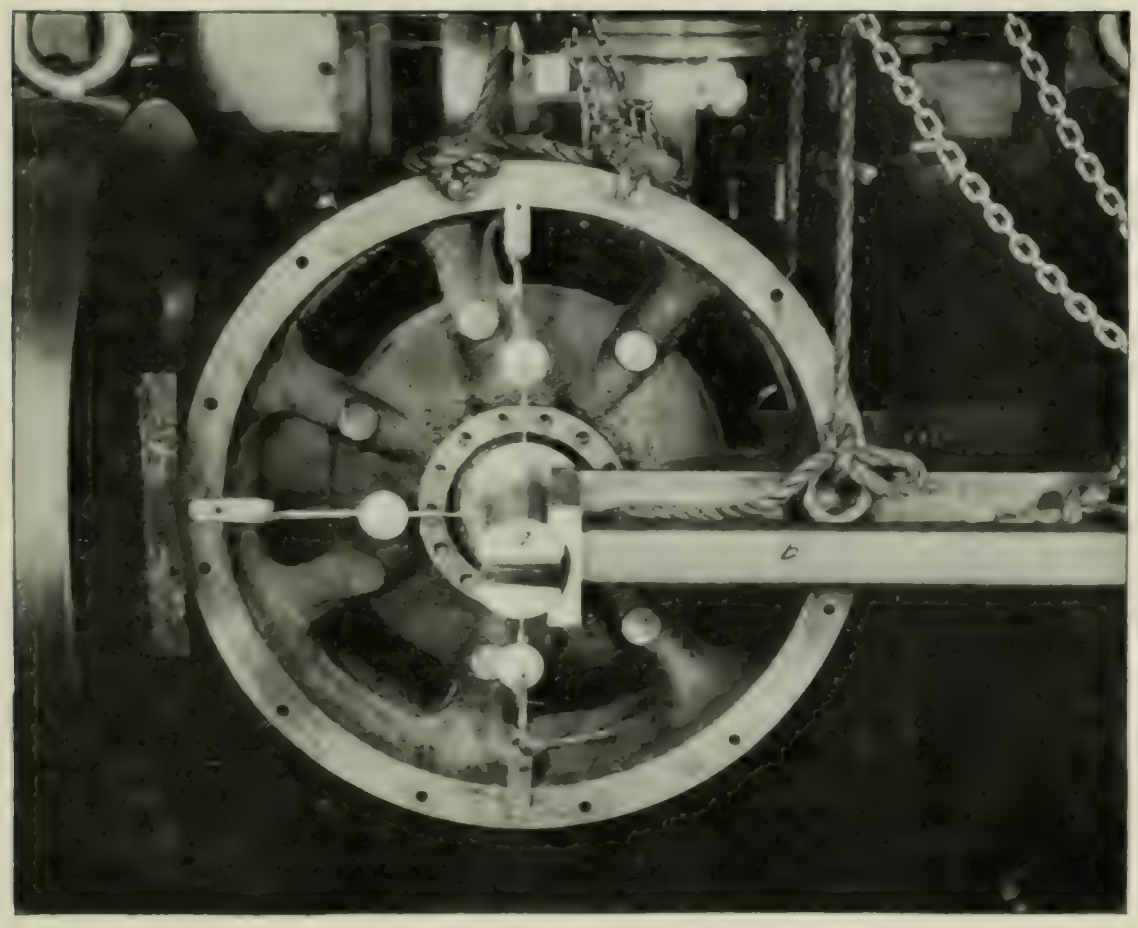

FIG. 1.—*Radial-compression test*

in Table 2. The data obtained from these tests are shown plotted as load-deformation curves.

In Table 2 are recorded the proportional limit of the wheel, as indicated by the measurements taken at the point of application of load; the maximum applied load; the deformation at maximum load; the permanent set due to stressing the wheel to the maximum load and the slope of the load-deformation curves.

**TABLE 2.—Radial Compression**

| Wheel No. | Proportional limit at load in pounds | Maximum applied load in pounds | Deformation at maximum load in pounds | Permanent set at maximum load in pounds | Slope of curve at load, 1000 pounds per inch |
|---|---|---|---|---|---|
| 1 | 38 000 | 60 000 | 0.1062 | 0.0336 | 826 000 |
| 2 | 31 000 | 60 000 | .0359 | .0187 | 2 450 000 |
| 3 | 50 000 | 100 000 | .0881 | .0261 | 1 891 000 |
| 4 | 34 000 | 60 000 | .0564 | .0072 | 1 238 000 |
| 5 | 85 000 | [a] 105 000 | .1631 | .0428 | 715 000 |
| 6 | 31 000 | 75 000 | .0847 | .0291 | 1 875 000 |
| 7 | 32 500 | 50 000 | .0490 | .0135 | 1 363 000 |
| 8 | 50 000 | 100 000 | .0610 | .0103 | 2 000 000 |
| 9 | 35 500 | 60 000 | .1287 | .0791 | 667 000 |
| 10 | 77 000 | 120 000 | .1250 | .0537 | 1 316 000 |
| 11 | 32 000 | 60 000 | .0695 | .0311 | 1 160 000 |
| 12 | 40 000 | 60 000 | .0645 | .0220 | 1 333 000 |
| 13 | 20 000 | 100 000 | .0513 | .0113 | 6 060 000 |
| 14 | 26 000 | 60 000 | .1135 | .0687 | 1 300 000 |
| 15 | 75 000 | 120 000 | .0874 | .0318 | 2 320 000 |
| 16 | 44 000 | 60 000 | .0744 | .0323 | 917 000 |
| 17 | 71 500 | 120 000 | .1586 | .0831 | 1 250 000 |
| 18 | 46 000 | 120 000 | .1230 | .0676 | 1 968 000 |
| 19 | 41 000 | 100 000 | .1555 | .1100 | 1 836 000 |
| 20 | 43 500 | 60 000 | .0741 | .0271 | 926 000 |
| 21 | 64 000 | 120 000 | .1361 | .0715 | 1 818 000 |

[a] Crack developed along rim of wheel where the two channels, of which the rim is formed, were welded.

The elastic resiliencies of the wheels have been computed for points Nos. 1, 2, 3, and 4 and recorded in Table 3. The area under the load-deformation curve from zero load to the proportional limit was here considered. In Table 3 will also be found the elastic resiliencies at load, per pound of metal in wheel.

**TABLE 3.—Radial Compression—Elastic Resiliencies**

[Area under load-deformation curves from zero to proportional limit]

| Wheel No. | No. 2 at load in inch-pounds | No. 1 90° from load in inch-pounds | No. 4 180° from load in inch-pounds | No. 3 270° from load in inch-pounds | At load per pound of metal in wheel in inch-pounds |
|---|---|---|---|---|---|
| 1 | 875 | ..... | 280 | 352 | 3.47 |
| 2 | 202 | ..... | ..... | ..... | 1.20 |
| 3 | 650 | 128 | 715 | 447 | 2.46 |
| 4 | 467 | ..... | ..... | ..... | 2.58 |
| 5 | 5050 | ..... | 725 | ..... | 14.3 |
| 6 | 257 | ..... | ..... | ..... | 1.2 |
| 7 | 387 | ..... | ..... | ..... | 2.89 |
| 8 | 625 | ..... | ..... | ..... | 2.28 |
| 9 | 1047 | 119 | ..... | 150 | 7.70 |
| 10 | 2250 | ..... | ..... | ..... | 7.00 |
| 11 | 441 | ..... | ..... | ..... | 3.06 |
| 12 | 600 | ..... | ..... | ..... | 4.6 |
| 13 | 33 | ..... | 390 | ..... | .1 |
| 14 | 260 | ..... | ..... | ..... | 1.97 |
| 15 | 1210 | ..... | 880 | ..... | 4.86 |
| 16 | 1056 | ..... | ..... | ..... | 8.80 |
| 17 | 2090 | 640 | 319 | 630 | 7.65 |
| 18 | 538 | ..... | ..... | ..... | 1.68 |
| 19 | 436 | 195 | ..... | 94 | 1.34 |
| 20 | 1131 | ..... | ..... | ..... | 8.02 |
| 21 | 1128 | ..... | 450 | 255 | 3.91 |

The proportional limit of a wheel is of importance not only because the rate of deformation does not remain constant beyond that point, but also because the wheel becomes permanently deformed if higher stresses are applied. Unless the yield point of the wheel has been reached, this permanent deformation in most cases is small and does not render the wheel unfit for further use. Note that the load-deformation curve above the proportional limit usually deviates but little from the line drawn through the points below the proportional limit. The maximum load applied to the wheels is not the ultimate or breaking load.

In general, only one front and one rear wheel of each type were submitted, and it was necessary to perform both the radial-compression and the side-thrust tests on the same wheel. No attempt was made, therefore, to break the wheel in the compression test. The load was increased, however, until the wheel had been stressed well beyond its proportional limit.

The slope of the load-deformation curve is an index of the stiffness of the wheel, a high value indicating a wheel which deforms but little for all loads below the proportional limit.

Recorded in Table 4 are the resiliences for various loads. These were computed from the curve of deformation for the point where the load was applied.

**TABLE 4.—Radial Compression—Resiliencies at Low Loads**

[Area under curve of deformations at load]

| Wheel No. | 2000 pounds in inch-pounds | 4000 pounds in inch-pounds | 6000 pounds in inch-pounds | 8000 pounds in inch-pounds | 10 000 pounds in inch-pounds | 12 000 pounds in inch-pounds | 14 000 pounds in inch-pounds | 16 000 pounds in inch-pounds | 18 000 pounds in inch-pounds | 20 000 pounds in inch-pounds |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 10 | 22 | 39 | 61 | 87 | 118 | 155 | 196 | 242 |
| 2 | 1 | 3 | 7 | 13 | 20 | 29 | 40 | 52 | 66 | 82 |
| 3 | 1 | 4 | 10 | 17 | 26 | 38 | 52 | 68 | 86 | 106 |
| 4 | 2 | 7 | 15 | 26 | 40 | 58 | 79 | 103 | 131 | 162 |
| 5 | 4 | 12 | 30 | 54 | 80 | 108 | 147 | 208 | 261 | 330 |
| 6 | 1 | 4 | 10 | 17 | 27 | 38 | 52 | 68 | 85 | 107 |
| 7 | 2 | 5 | 13 | 24 | 37 | 53 | 72 | 94 | 119 | 147 |
| 8 | 1 | 4 | 9 | 16 | 25 | 36 | 49 | 64 | 81 | 100 |
| 9 | 5 | 18 | 36 | 64 | 95 | 138 | 182 | 240 | 297 | 350 |
| 10 | 5 | 17 | 37 | 64 | 95 | 132 | 168 | 208 | 261 | 310 |
| 11 | 2 | 7 | 16 | 28 | 43 | 62 | 84 | 110 | 140 | 173 |
| 12 | 2 | 6 | 14 | 24 | 38 | 54 | 74 | 96 | 122 | 150 |
| 13 | ..... | 1 | 3 | 5 | 8 | 12 | 16 | 21 | 27 | 33 |
| 14 | 2 | 6 | 14 | 25 | 39 | 55 | 75 | 98 | 125 | 154 |
| 15 | 1 | 4 | 8 | 14 | 22 | 31 | 42 | 55 | 70 | 86 |
| 16 | 2 | 9 | 20 | 35 | 55 | 79 | 107 | 140 | 177 | 218 |
| 17 | 2 | 6 | 14 | 26 | 40 | 58 | 78 | 102 | 130 | 160 |
| 18 | 1 | 4 | 9 | 16 | 26 | 37 | 50 | 65 | 82 | 102 |
| 19 | 1 | 4 | 10 | 17 | 27 | 39 | 53 | 70 | 88 | 109 |
| 20 | 4 | 16 | 33 | 56 | 80 | 108 | 140 | 176 | 221 | 270 |
| 21 | 1 | 4 | 10 | 18 | 28 | 40 | 54 | 70 | 89 | 110 |

The elastic resiliences recorded in Table 3 afford another means of comparison. They should not be used, however, without at the same time carefully considering the other qualities of the wheel. Large elastic resiliency is desirable, but it may be large only because of the high proportional limit of the wheel and not because of large elastic deformation. In such cases the resiliency would be small at the loads to which the wheel is ordinarily subjected. The resiliencies at low loads were therefore computed. These resiliencies at low loads may or may not be a proportional part of the total elastic resiliency. In many cases the slope of the load-deformation curve is not a constant at low loads. This is probably due to strains being localized at first and the wheel not acting as a unit. There may also have been some movement necessary to bring the axle and bushings to a firm bearing. This movement would be recorded as deformation in the wheel because the measurements were made between the rim and the axle.

## VI. SIDE-THRUST TEST

Each wheel was subjected to a side-thrust or skid test after it had been tested in radial compression.

The wheel was placed on the same axle as in the radial-compression test. As shown in Fig. 3 (frontispiece) one end of the axle was passed through a 1⅛-inch plate and then through the web of an 8½-inch, 90½-pound Bethlehem H beam to which the plate was fastened. The other end was tied back to the H beam with a 1¼-inch round bar. In this manner an effort was made to hold the axle rigidly, with its axis perpendicular to the side of the H beam, while load was applied to a section of the side of the rim of the wheel.

The wheel, mounted on the H beam, was then placed in the testing machine. The side of the H beam was supported by one head of the machine and the axis of the axle was parallel to the axis of the testing machine and, therefore, parallel to the direction of the applied load. This load was applied to the side of the rim of the wheel at point (*a*) through a block 6 inches wide. The wheel was so placed that the point of application of load was between spokes and approximately 90° from the point at which the stress had been applied in the radial-compression test. To measure the deformation of the wheel under load, Ames dials were fastened between the H beam and the side of the rim of the wheel at the point where the load was to be applied, and at a point diametrically opposite.

In this test the wheels were loaded to destruction.

Load-deflection curves were plotted, and are shown with the radial-compression curves.

In Table 5 are listed the proportional limits, the ultimate strengths, and the slopes of the curves.

**TABLE 5.—Side Thrust**

| Wheel No. | Proportional limit at load in pounds | Ultimate load in pounds | Slope of curve at load, 1000 pounds per inch | Wheel No. | Proportional limit at load in pounds | Ultimate load in pounds | Slope of curve at load, 1000 pounds per inch |
|---|---|---|---|---|---|---|---|
| 1 | 18 000 | 43 700 | 45 200 | 12 | 16 500 | 49 200 | 74 800 |
| 2 | 12 000 | 48 100 | 54 000 | 13 | 38 000 | 101 000 | 179 000 |
| 3 | 36 500 | 75 500 | 131 300 | 14 | 10 500 | 34 000 | 63 700 |
| 4 | 6 000 | 19 000 | 38 500 | 15 | 37 500 | 68 000 | 107 100 |
| 5 | 10 000 | 25 000 | 45 200 | 16 | 14 000 | 30 200 | 43 000 |
| 6 | 15 500 | 54 000 | 101 300 | 17 | 40 000 | 60 600 | 104 000 |
| 7 | 13 000 | 31 100 | 52 500 | 18 | 35 000 | 82 300 | 93 200 |
| 8 | 34 500 | 65 000 | 131 500 | 19 | 31 000 | 59 300 | 67 100 |
| 9 | 7 500 | 26 700 | 36 400 | 20 | 12 500 | 25 300 | 45 400 |
| 10 | 35 000 | 81 700 | 125 000 | 21 | 28 000 | 55 400 | 69 600 |
| 11 | 13 000 | 39 300 | 58 100 | | | | |

The elastic resiliencies and the elastic resiliencies per pound of metal in wheel loads are recorded in Table 6.

**TABLE 6.—Side Thrust—Resiliencies at Low Loads**

[Area under load-deformation curve from zero to proportional limit]

| Wheel No. | At load in inch-pounds | 180° from load in inch-pounds | At load per pound of metal in wheel in inch-pounds | Wheel No. | At load in inch-pounds | 180° from load in inch-pounds | At load per pound of metal in wheel in inch-pounds |
|---|---|---|---|---|---|---|---|
| 1 | 3185 | 1800 | 12.65 | 12 | 1820 | 1480 | 14.00 |
| 2 | 1333 | 950 | 7.90 | 13 | 4040 | 5170 | 14.20 |
| 3 | 5060 | 2640 | 18.90 | 14 | 865 | 330 | 6.55 |
| 4 | 468 | 575 | 2.58 | 15 | 6550 | 6480 | 26.30 |
| 5 | 1108 | 618 | 3.15 | 16 | 2280 | 700 | 19.00 |
| 6 | 1185 | 1470 | 5.51 | 17 | 7680 | 850 | 20.30 |
| 7 | 1610 | 595 | 12.00 | 18 | 6960 | 4900 | 20.20 |
| 8 | 4520 | 2880 | 16.50 | 19 | 7160 | 7700 | 22.00 |
| 9 | 772 | 413 | 5.67 | 20 | 1718 | 310 | 12.20 |
| 10 | 5440 | 4100 | 16.90 | 21 | 7280 | ..... | 25.30 |
| 11 | 1460 | 1680 | 10.10 | | | | |

The resiliencies for various loads were computed from the curve of deflection at the point of application of load and are recorded in Table 7.

**TABLE 7.—Side Thrust—Resiliencies at Low Loads**

[Area under curve of deformation at load]

| Wheel No. | 2000 pounds in inch-pounds | 4000 pounds in inch-pounds | 6000 pounds in inch-pounds | 8000 pounds in inch-pounds | 10 000 pounds in inch-pounds | 12 000 pounds in inch-pounds | 14 000 pounds in inch-pounds | 16 000 pounds in inch-pounds | 18 000 pounds in inch-pounds | 20 000 pounds in inch-pounds |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 45 | 177 | 398 | 708 | 1105 | 1590 | 2170 | 2830 | 3580 | ..... |
| 2 | 37 | 148 | 333 | 593 | 927 | 1332 | ..... | ..... | ..... | ..... |
| 3 | 15 | 61 | 137 | 244 | 381 | 549 | 746 | 976 | 1232 | 1523 |
| 4 | 52 | 208 | 469 | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| 5 | 44 | 177 | 398 | 708 | 1109 | ..... | ..... | ..... | ..... | ..... |
| 6 | 20 | 79 | 177 | 316 | 494 | 710 | 966 | ..... | ..... | ..... |
| 7 | 38 | 152 | 343 | 610 | 954 | 1371 | ..... | ..... | ..... | ..... |
| 8 | 15 | 61 | 137 | 243 | 380 | 548 | 746 | 973 | 1232 | 1521 |
| 9 | 55 | 220 | 494 | 879 | ..... | ..... | ..... | ..... | ..... | ..... |
| 10 | 20 | 86 | 180 | 320 | 500 | 720 | 980 | 1280 | 1530 | 1900 |
| 11 | 35 | 138 | 310 | 551 | 860 | 1235 | ..... | ..... | ..... | ..... |
| 12 | 27 | 107 | 241 | 428 | 668 | 963 | 1310 | 1710 | ..... | ..... |
| 13 | 11 | 45 | 105 | 179 | 279 | 402 | 547 | 714 | 903 | 1116 |
| 14 | 31 | 126 | 282 | 502 | 785 | ..... | ..... | ..... | ..... | ..... |
| 15 | 19 | 75 | 168 | 299 | 468 | 672 | 914 | 1195 | 1512 | 1866 |
| 16 | 47 | 186 | 418 | 744 | 1160 | 1675 | 2280 | ..... | ..... | ..... |
| 17 | 19 | 77 | 173 | 308 | 481 | 693 | 943 | 1232 | 1558 | 1924 |
| 18 | 21 | 86 | 193 | 343 | 536 | 772 | 1050 | 1374 | 1740 | 2146 |
| 19 | 30 | 119 | 269 | 477 | 745 | 1073 | 1460 | 1906 | 2413 | 2975 |
| 20 | 44 | 176 | 396 | 705 | 1100 | 1584 | ..... | ..... | ..... | ..... |
| 21 | 70 | 270 | 555 | 900 | 1300 | 1740 | 2240 | 2760 | 3380 | 4000 |

The character of the failure due to side thrust will be found on the summary sheet for each wheel.

In the majority of tests failure occurred in the spokes, near the hub. This was to be expected because of the large bending moment at that section.

As indicated by the load-deflection curves, large stresses are transmitted through the rim to the portion of the wheel diametrically opposite to that on which the load is applied.

To obtain the actual deformation of the wheel it would be necessary to make a correction due to the bending of the axle. Comparative results only were required and, except in a few tests, no attempt was made to measure the bending of the axle.

In these tests the deflection of the axle was measured at a point which was at the same distance from the support as the deflection points on the edge of the rim. In this way, for a given load the actual deformation of the wheel, either at the point where the load is applied or at the diametrically opposite point, is obtained by subtracting the deflection of the axle from the total deflection of the wheel.

Each load-deflection curve of the axle is shown plotted with the other curves of the test in which the deflection was measured.

As previously stated, the proportional limit is the point at which the rate of deformation changes, and beyond which the wheel becomes permanently deformed. The slope of the load-deformation curve is a measure of the stiffness of the wheel for loads below the proportional limit.

The initial deviation of the load-deformation curve from a straight line is more pronounced here than in the radial-compression tests and again is probably due to localization of strains and to bringing the axle and bushings to a firm bearing.

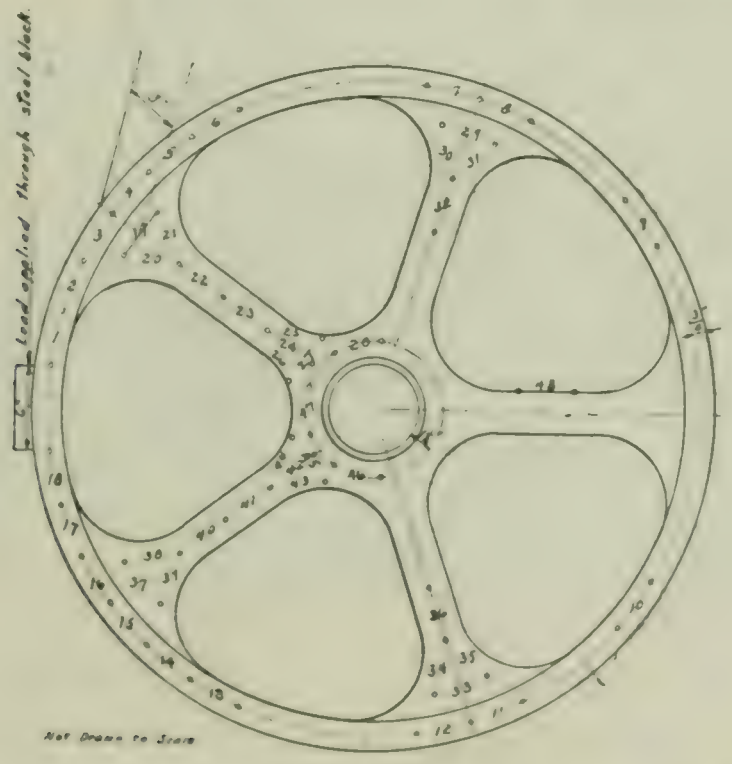

FIG. 4.—*Location of strain gage points, cast-steel, hollow-spoke wheel*

## VII. DISTRIBUTION OF STRESS IN WHEEL

An attempt was made to determine the distribution of stress in a wheel under radial-compressive loads. Wheel No. 11, the cast-steel wheel having five hollow spokes, was the only one available at the time, so it was used for the test.

Strain-gage lines were located and numbered as shown on Fig. 4. They were symmetrically placed on either side of a line through the center of the loading block and the center of the wheel. The lines were 2 inches in length, their ends being marked by small holes made with a No. 56 twist drill.

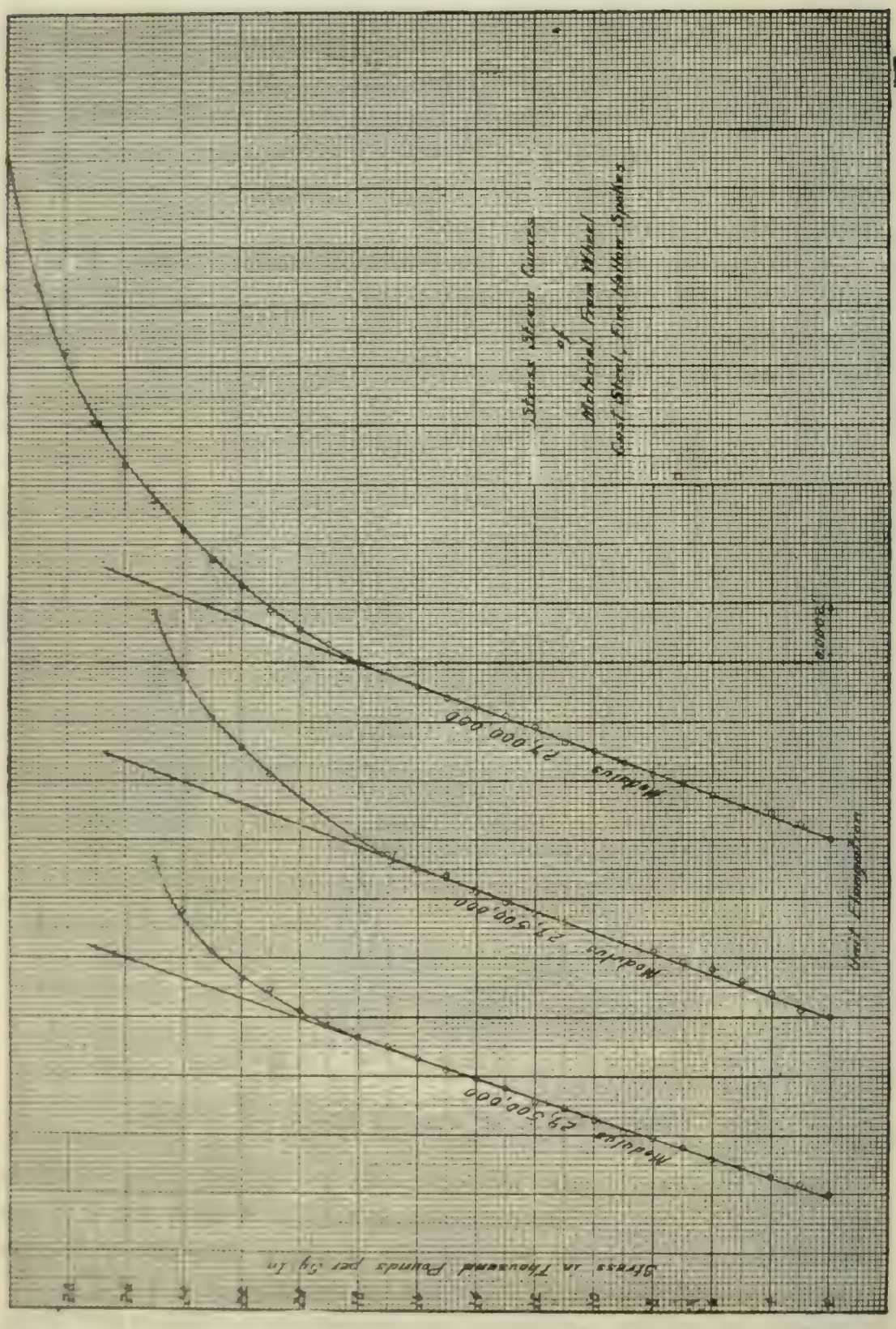


FIG. 5.—*Stress-strain curves of material for cast-steel wheel with five hollow spokes*

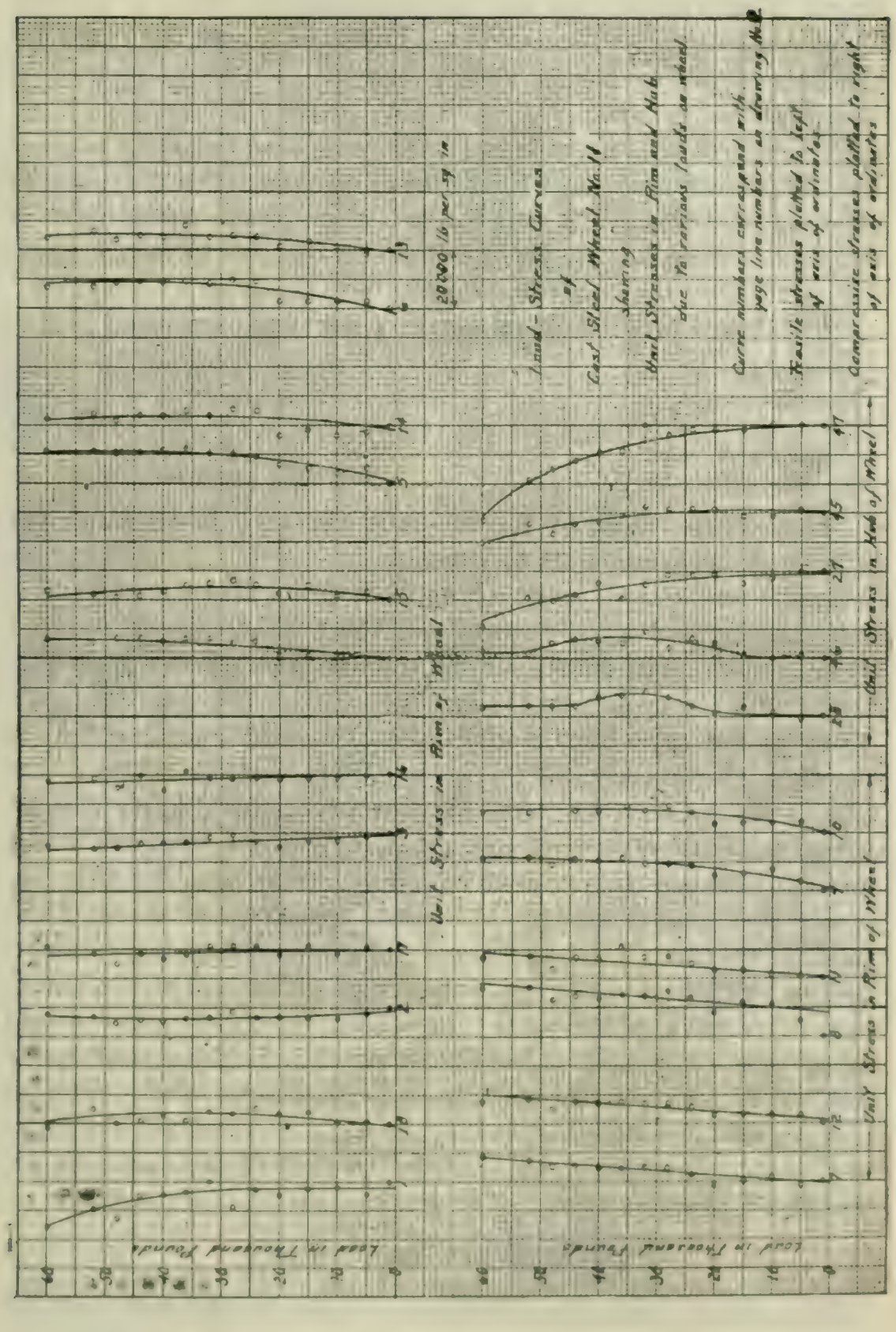
Load – Stress Curves
of
Cast Steel Wheel No. 11
showing
Unit Stresses in Rim and Hub
due to various loads on wheel
Curve numbers correspond with
page line numbers on drawing No.
Tensile stresses plotted to left
of axis of ordinates
Compressive stresses plotted to right
of axis of ordinates
Load in Thousand Pounds
Unit Stress in Rim of Wheel
Unit Stress in Hub of Wheel
20000 lb per sq in

FIG. 6.—*Load-stress curves, wheel No. 11, showing stresses in rim and hub*

The wheel was subjected to a radial-compressive test as described in Section V. At each load increment the change in length of each strain-gage line was measured by means of a 2-inch Berry strain gage. The smallest change in length indicated by the gage dial was 0.0002 inch. Changes of 0.00002 inch could be estimated.

The reduction of these linear measurements to stresses necessitated the determination of the modulus of elasticity of the material of which the wheel was constructed. Specimens were therefore cut from the spokes of the wheel and subjected to tensile tests. The results are shown plotted on Fig. 5.

The average mechanical properties determined are listed below:

| | | |
|---|---|---|
| Ultimate strength | pounds per square inch | 61 000 |
| Proportional limit | do | 17 700 |
| Reduction in area | per cent | 17.3 |
| Elongation in 2 inches | do | 12.0 |
| Modulus of elasticity | pounds per square inch | 28 000 000 |

This average value of the modulus was used in reducing the strain-gage measurements to stresses.

Load-stress curves were then plotted to show the relation between the load on the wheel and the unit stresses introduced by that load. The curves for the rim and hub are shown on Fig. 6, those for the spokes on Fig. 7.

Curves for gage lines similarly located, with reference to the line through the center of the loading block and the center of the wheel, were plotted in pairs. These curves check fairly closely. Exact duplication was not to be expected as the curves show the relation between applied load and unit stress, and not that between the applied load and the load transmitted through the section, so that, while the loads transmitted through symmetrically located sections are equal, any difference in the thickness or other dimensions of the casting at these points would result in a difference in the unit stresses. For example, spoke sections 22 and 40 will each transmit equal parts of any external load applied through the loading block. If, however, the cross section of the spoke at 22 is less than that of the spoke at 40, then the unit stress at 22 will be greater than the unit stress at 40

### 1. STRESSES IN RIM OF WHEEL

It is evident from the load-stress curves for the rim that the circumferential stresses do not exceed the proportional limit of the material (17 700 pounds per square inch) for any load on the wheel up to 60 000 pounds.

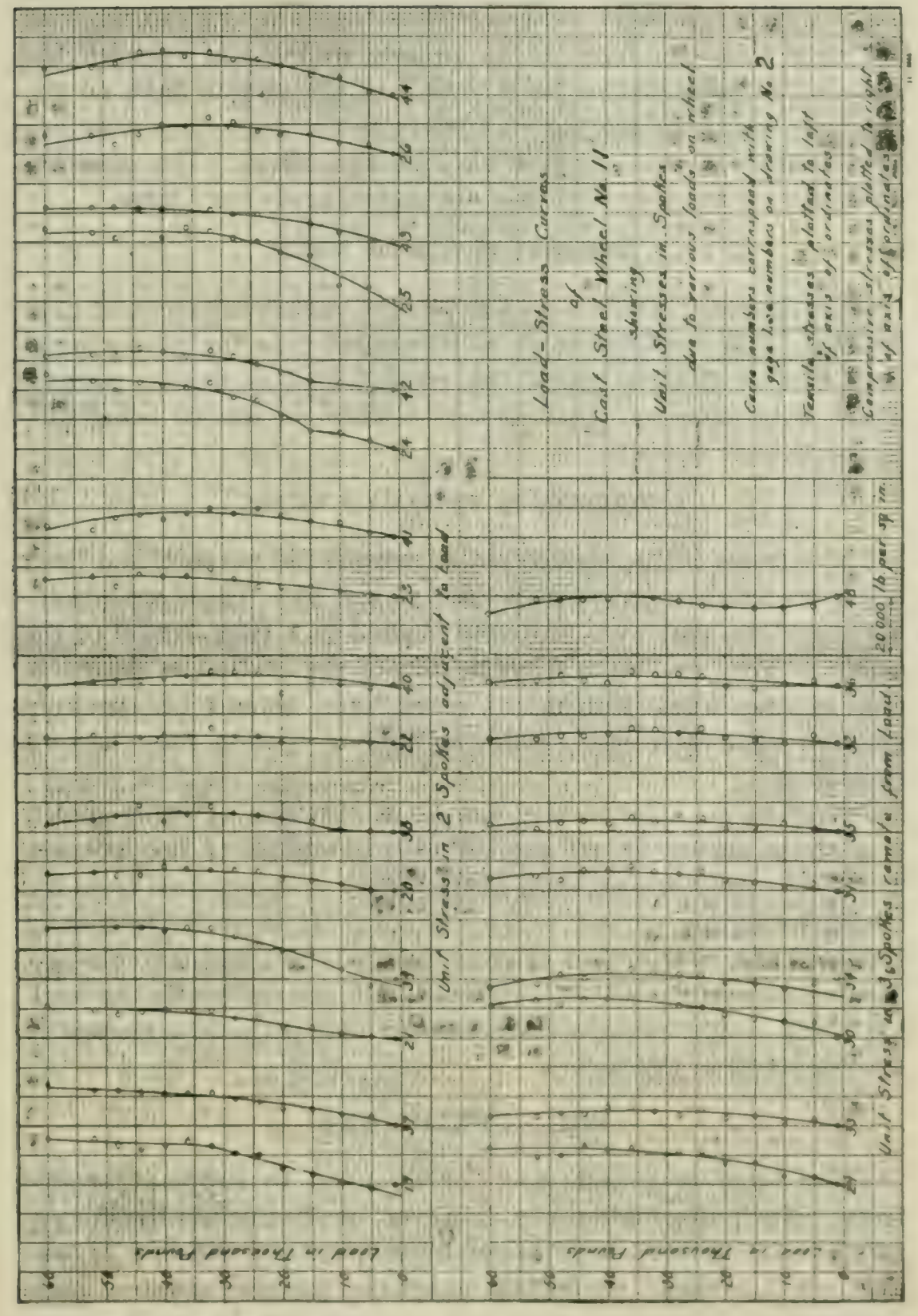
Load-Stress Curves
of
Cast Steel Wheel No. 11
showing
Unit Stresses in Spokes
due to various loads on wheel
Curve numbers correspond with
gage location on drawing No. 2
Tensile stresses plotted to left
of axis of ordinates
Compressive stresses plotted to right
Load in Thousand Pounds
Unit Stress in 2 Spokes adjacent to Load
Unit Stress in 6 Spokes remote from Load
20000 lb per sq in.

FIG. 7.—*Load-stress curves, wheel No. 11, showing stresses in spokes*

These stresses are compressive in all parts of the rim except in the section between the spokes adjacent to the loading block. These spokes are inclined in the direction of the applied load, and the circumferential components of their reactions to the load are such as to produce tensile stresses in the rim between the spokes. Stresses due to beam action in the section have no appreciable effect on the measurements as the gage lines were approximately on the neutral axis of the beam. The shearing stresses were not measured but are undoubtedly very large.

### 2. STRESSES IN HUB OF WHEEL

The stresses in the hub do not become excessive except at gage line 47. The tensile stresses at this point pass the proportional limit of the material when the applied load is 50 000 pounds. There is, however, no possibility of a wheel in service being subjected to such a load.

### 3. STRESSES IN SPOKES OF WHEEL

The stresses in the spokes are all within the porportional limit of the material except at gage lines 24 and 25. These are adjoining gage lines and were probably located in a thin section of the casting. Any reduction from section of the casting as designed, due to blowholes, shifting of cores, etc., should be carefully guarded against as the strains in such a section may become excessive.

Attention is called to the change in direction of many of the load-stress curves at an applied load of about 32 000 pounds. This is the proportional limit of the wheel as determined from the load-deformation curves. (See Fig. 18.) It is probable that at this load the distribution of stress in the wheel began to change. The increase in the rate of deformation of the rim under the loading block would cause a readjustment and perhaps a change in kind of stress in the spokes.

## VIII. CONCLUSIONS

These laboratory tests are not intended to supplant service tests. Much information can, however, be obtained in the laboratory which could not be obtained by service tests within a reasonable length of time. Defects in design and material are soon made apparent in laboratory tests and changes can be made before wheels are manufactured in large quantities.

The wheels tested were representative of those used on 3 and 5 ton trucks, and it is quite improbable that any of these wheels would ever be stressed even to its proportional limit.

The wheels tested are all stronger and heavier than is necessary, and a saving in material should be effected.

A reduction in weight is worthy of consideration, not only because of the material saved, but also because it would result in an increase in the life of tires and of roads.

## IX. SUMMARY SHEETS AND CURVES

In the following pages are recorded the results of the tests.

Each summary sheet contains all of the information obtained from the tests on a single wheel. On the page facing the summary sheet are the load-deformation curves for that wheel.

## TABLE 8.—Wheel No. 1

[Description—Rear wheel, 36 by 10 inches; wood, 14 spokes. Weight—252 pounds]

### RADIAL-COMPRESSION TESTS

| | |
|---|---|
| Proportional limit in pounds | 38 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.1062 |
| Permanent set at maximum load in inches | 0.0336 |
| Slope of curve No. 2 in pounds per inch | 826 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 875 |
| 270° from load | 352 |
| 180° from load | 230 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 3.47 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 10 |
| 6000 pounds | 22 |
| 8000 pounds | 39 |
| 10 000 pounds | 61 |
| 12 000 pounds | 87 |
| 14 000 pounds | 118 |
| 16 000 pounds | 155 |
| 18 000 pounds | 196 |
| 20 000 pounds | 242 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 18 000 |
| Ultimate strength in pounds | 43 700 |
| Slope of curve in pounds per inch | 45 200 |
| Elastic resiliency in inch-pounds: | |
| At load | 3185 |
| 180° from load | 1800 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 12.65 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 45 |
| 4000 pounds | 117 |
| 6000 pounds | 398 |
| 8000 pounds | 708 |
| 10 000 pounds | 1105 |
| 12 000 pounds | 1590 |
| 14 000 pounds | 2170 |
| 16 000 pounds | 2830 |
| 18 000 pounds | 3580 |

Character of failure: Failed by splitting of spokes near point of application of load and at 180° from that point. Six spokes split near point of application of load. Four spokes split at 180° from point of application of load. Felly moved one-half inch along spokes at point of application of load.

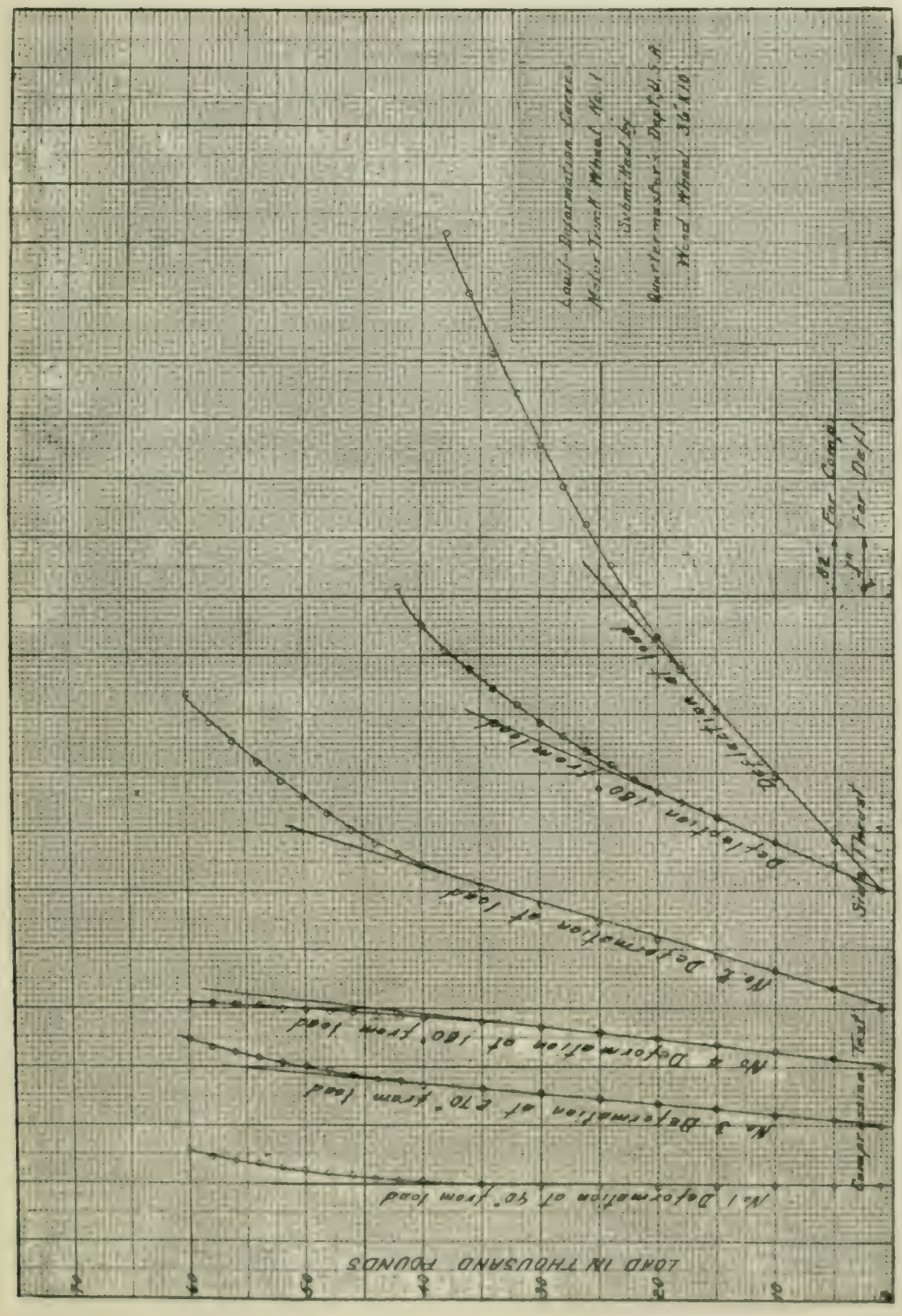


FIG. 8.—*Load-deformation curves, wheel No. 1*

## TABLE No. 9.—Wheel No. 2

[Description—Front wheel, 36 by 5 inches; cast-steel disk, box rim. Weight—169 pounds. Chemical analysis (per cent)—Carbon, 0.34; sulphur, 0.048; phosphorus, 0.039; manganese, 0.61; silicon, 0.35]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 31 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0359 |
| Permanent set at maximum load in inches | 0.0187 |
| Slope of curve No. 2 in pounds per inch | 2 450 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 202 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 1.20 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 3 |
| 6000 pounds | 7 |
| 8000 pounds | 13 |
| 10 000 pounds | 20 |
| 12 000 pounds | 29 |
| 14 000 pounds | 40 |
| 16 000 pounds | 52 |
| 18 000 pounds | 66 |
| 20 000 pounds | 82 |

### SIDE-THURST TEST

| | |
|---|---|
| Proportional limit in pounds | 12 000 |
| Ultimate strength in pounds | 48 100 |
| Slope of curve in pounds per inch | 54 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 1333 |
| 180° from load | 980 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 7.90 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 37 |
| 4000 pounds | 148 |
| 6000 pounds | 333 |
| 8000 pounds | 593 |
| 10 000 pounds | 927 |
| 12 000 pounds | 1332 |

Character of failure: Failed by bending of entire wheel. No signs of rupture in material except small cracks in felly.

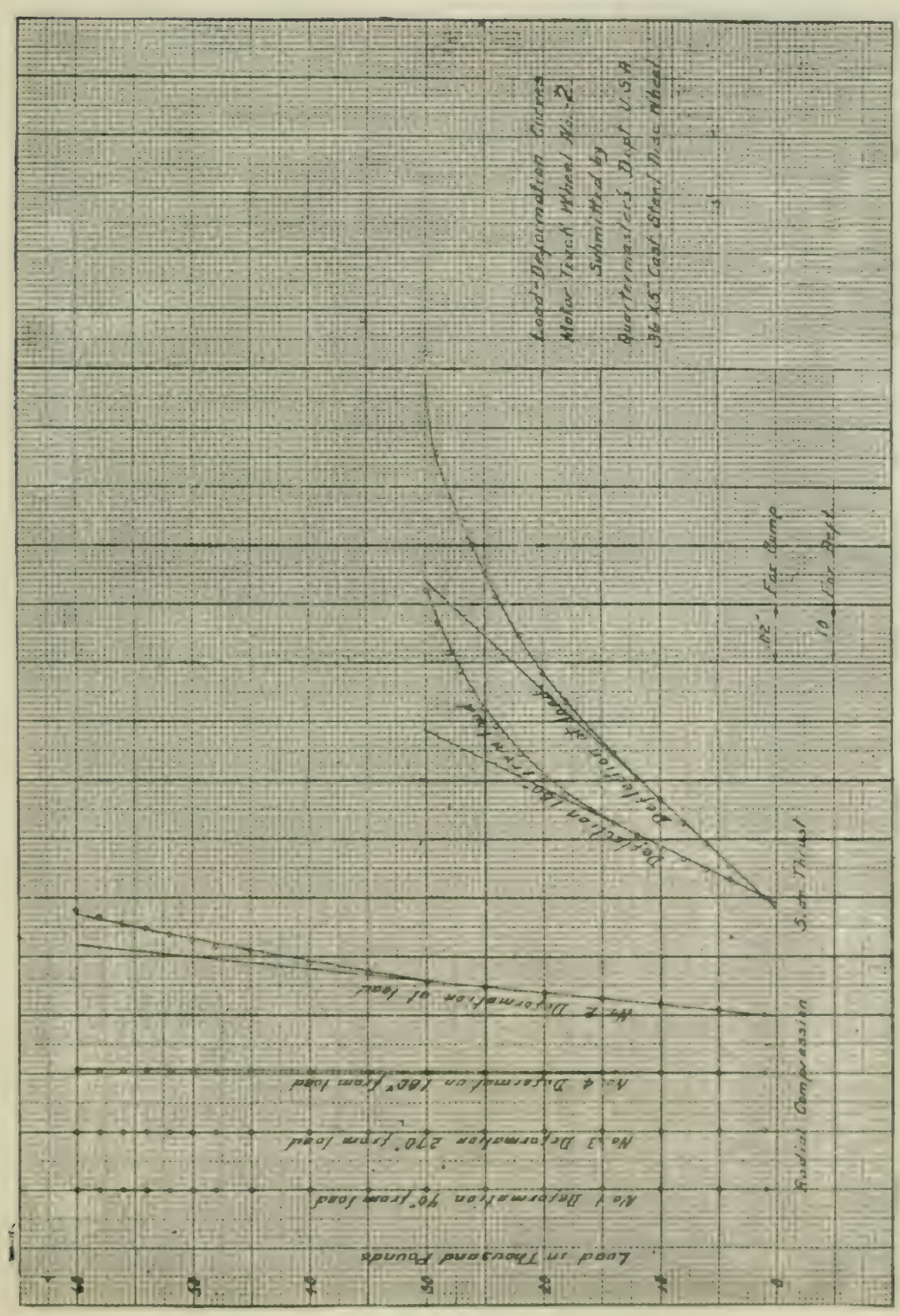


FIG. 9 *Load-deformation curves, wheel No. 2*

## TABLE 10.—Wheel No. 3

[Description—Rear wheel, 36 by 10 inches; cast-steel disk; box rim. Weight—268 pounds. Chemical analysis (per cent)—Carbon, 0.33; sulphur, 0.051; phosphorus, 0.046; manganese, 0.74; silicon, 0.36]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 50 000 |
| Maximum applied load in pounds | 100 000 |
| Deformation at maximum load in inches | 0.0881 |
| Permanent set at maximum load in inches | 0.0261 |
| Slope of curve No. 2 in pounds per inch | 1 891 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | 128 |
| At load | 660 |
| 270° from load | 447 |
| 180° from load | 715 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 2.46 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 10 |
| 8000 pounds | 17 |
| 10 000 pounds | 26 |
| 12 000 pounds | 38 |
| 14 000 pounds | 52 |
| 16 000 pounds | 68 |
| 18 000 pounds | 86 |
| 20 000 pounds | 106 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 36 500 |
| Ultimate strength in pounds | 75 500 |
| Slope of curve in pounds per inch | 131 300 |
| Elastic resiliency in inch-pounds: | |
| At load | 5060 |
| 180° from load | 2640 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 18.90 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 15 |
| 4000 pounds | 61 |
| 6000 pounds | 137 |
| 8000 pounds | 244 |
| 10 000 pounds | 381 |
| 12 000 pounds | 549 |
| 14 000 pounds | 746 |
| 16 000 pounds | 976 |
| 18 000 pounds | 1232 |
| 20 000 pounds | 1523 |

Character of failure: Failed by bending of entire wheel. Below point of application of load a crack 6 inches long ran from circumference of wheel toward the hub. Tension hair cracks developed along arc of 180° at bottom of slope from hub.

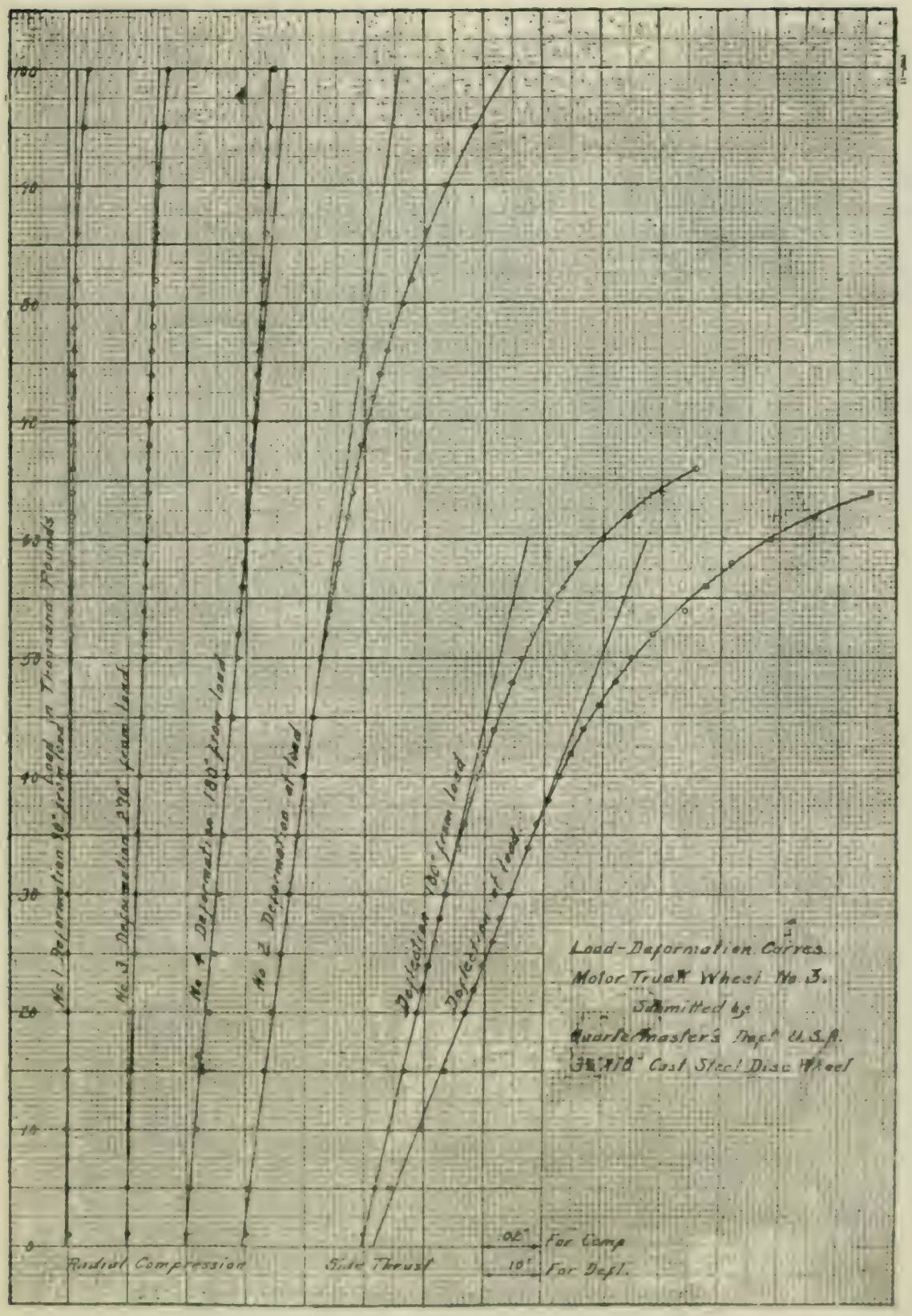


FIG. 10.—*Load-deformation curves, wheel No. 3*

## TABLE 11.—Wheel No. 4

[Description—Front wheel, 40 by 6 inches; pressed steel, corrugated web; channel iron rim. Weight—181 pounds. Chemical analysis (per cent.)

| | Hub | Web | Rim |
|---|---|---|---|
| Carbon | 0.19 | 0.15 | 0.11 |
| Sulphur | 0.046 | 0.063 | 0.050 |
| Phosphorus | 0.030 | 0.044 | 0.092 |
| Manganese | 0.59 | 0.48 | 0.40 |
| Silicon | 0.28 | 0.02 | 0.02] |

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 34 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0564 |
| Permanent set at maximum load in inches | 0.0072 |
| Slope of curve No. 2 in pounds per inch | 1 238 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 467 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 2.58 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 7 |
| 6000 pounds | 15 |
| 8000 pounds | 26 |
| 10 000 pounds | 40 |
| 12 000 pounds | 58 |
| 14 000 pounds | 79 |
| 16 000 pounds | 103 |
| 18 000 pounds | 131 |
| 20 000 pounds | 162 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 6000 |
| Ultimate strength in pounds | 19 000 |
| Slope of curve in pounds per inch | 385 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 468 |
| 180° from load | 575 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 2.58 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 52 |
| 4000 pounds | 208 |
| 6000 pounds | 469 |

Character of failure: Failed by web pulling from hub.

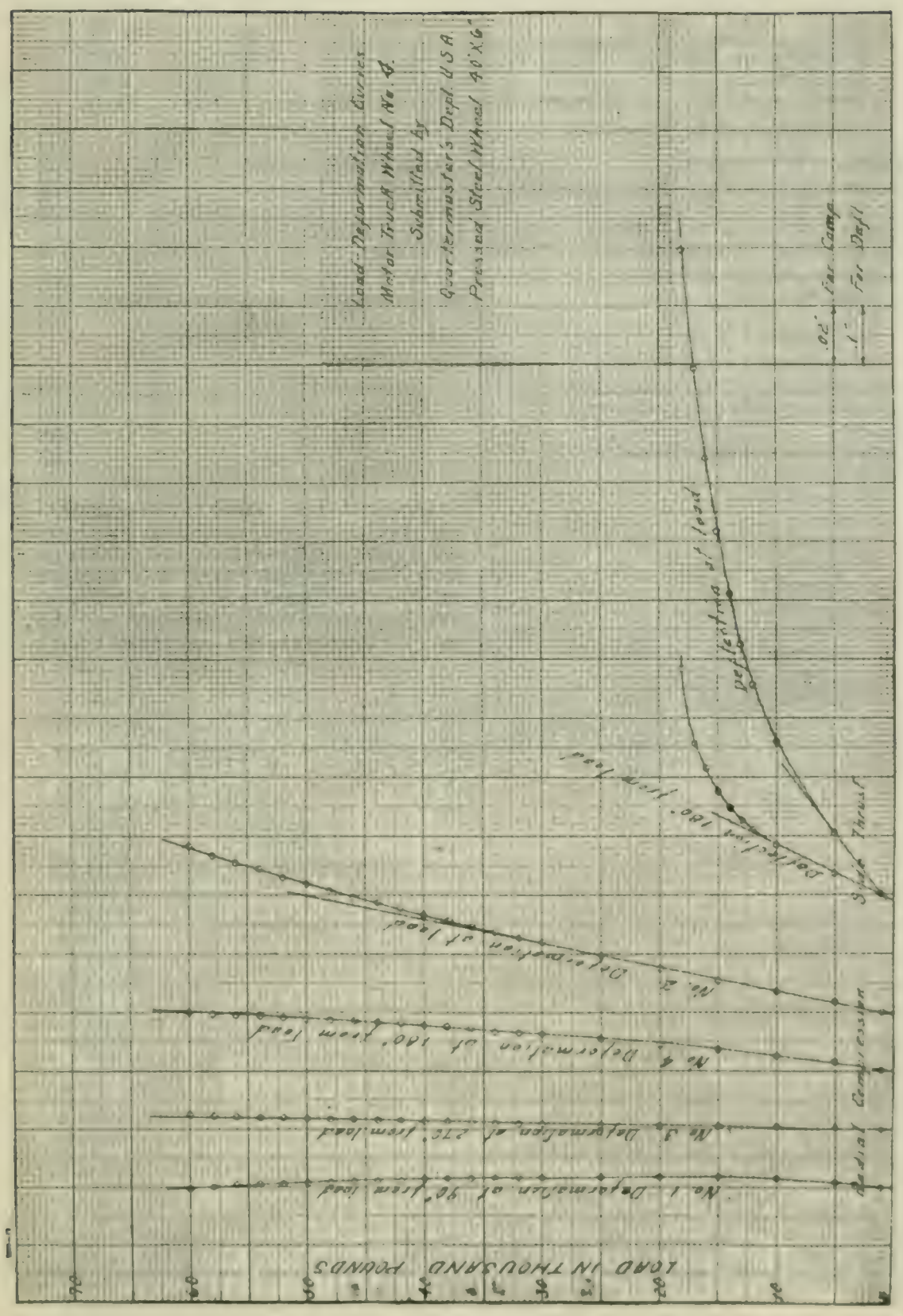


FIG. 11.—*Load deformation curves, wheel No. 4*

## TABLE 12.—Wheel No. 5

[Description—Rear wheel, 40 by 12 inches; pressed steel, corrugated web; channel iron rim. Weight—354 pounds. Chemical analysis (per cent)

| | Hub | Web | Rim |
|---|---|---|---|
| Carbon | 0.19 | 0.15 | 0.11 |
| Sulphur | 0.046 | 0.063 | 0.050 |
| Phosphorus | 0.030 | 0.044 | 0.092 |
| Manganese | 0.59 | 0.48 | 0.40 |
| Silicon | 0.28 | 0.02 | 0.02] |

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 85 000 |
| Maximum applied load in pounds | [a] 105 000 |
| Deformation at maximum load in inches | 0.1631 |
| Permanent set at maximum load in inches | 0.0428 |
| Slope of curve No. 2 in pounds per inch | 715 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 5050 |
| 270° from load | |
| 180° from load | 725 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 14.3 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 4 |
| 4000 pounds | 12 |
| 6000 pounds | 30 |
| 8000 pounds | 54 |
| 10 000 pounds | 80 |
| 12 000 pounds | 108 |
| 14 000 pounds | 147 |
| 16 000 pounds | 208 |
| 18 000 pounds | 261 |
| 20 000 pounds | 330 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 10 000 |
| Ultimate strength in pounds | 25 000 |
| Slope of curve in pounds per inch | 45 200 |
| Elastic resiliency in inch-pounds: | |
| At load | 1108 |
| 180° from load | 618 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 3.15 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 44 |
| 4000 pounds | 177 |
| 6000 pounds | 398 |
| 8000 pounds | 708 |
| 10 000 pounds | 1109 |

Character of failure: Failed by web pulling from hub. Failure was more pronounced at 90° from the load than it was at the point where the load was applied. This was probably due to the crack in the rim of the wheel (caused by parting of channel irons) which had developed during the radial compression test. The brake band pulled away from the web.

[a] Crack developed along rim of wheel where the two channels, of which the rim is formed, were welded.

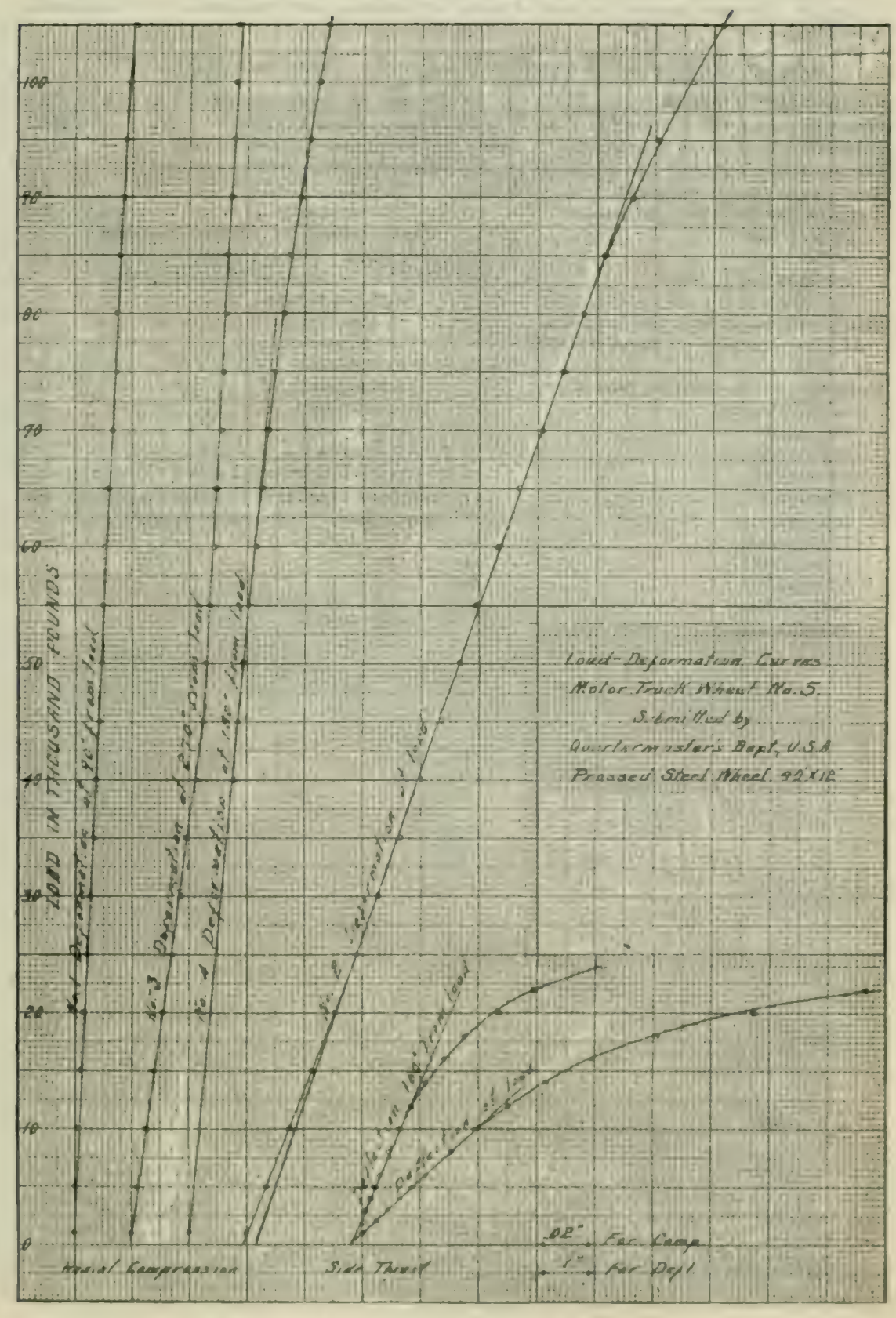


FIG. 12.—*Load-deformation curves, wheel No. 5*

## TABLE 13.—Wheel No. 6

[Description—Rear wheel, 36 by 6 inches; cast steel; 8+ spokes; brake band cast on wheel. Weight—215 pounds. Chemical analysis (per cent)—Carbon, 0.19; sulphur, 0.083; phosphorus, 0.054; manganese, 0.64; silicon, 0.35]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 31 000 |
| Maximum applied load in pounds | 75 000 |
| Deformation at maximum load in inches | 0.0847 |
| Permanent set at maximum load in inches | 0.0291 |
| Slope of curve No. 2 in pounds per inch | 1 875 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 257 |
| 270° from load | |
| 180° from load | |
| Elastic resiliency in inch-pounds at point of application of load, per pound of metal in wheel | 1.20 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 10 |
| 8000 pounds | 17 |
| 10 000 pounds | 27 |
| 12 000 pounds | 38 |
| 14 000 pounds | 52 |
| 16 000 pounds | 68 |
| 18 000 pounds | 86 |
| 20 000 pounds | 107 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 15 500 |
| Ultimate strength in pounds | 54 000 |
| Slope of curve in pounds per inch | 101 300 |
| Elastic resiliency in inch-pounds: | |
| At load | 1185 |
| 180° from load | 1470 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 5.51 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 20 |
| 4000 pounds | 79 |
| 6000 pounds | 177 |
| 8000 pounds | 316 |
| 10 000 pounds | 494 |
| 12 000 pounds | 710 |
| 14 000 pounds | 966 |

Character of failure: Tension failure at root of four spokes near point of application of load. Also tension failure in rim near same point.

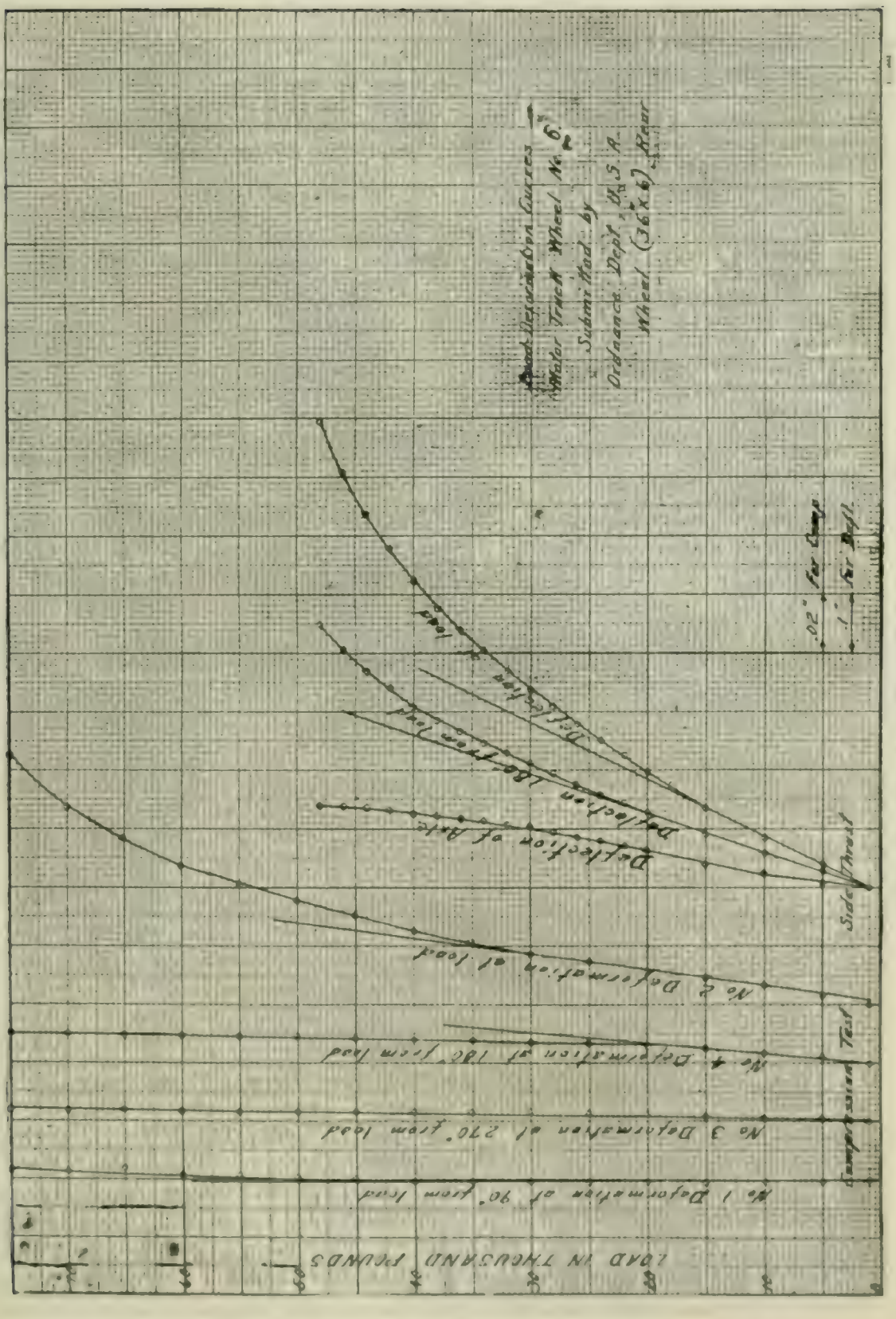


FIG. 13.—*Load-deformation curves, wheel No. 6*

## TABLE 14.—Wheel No. 7

[Description—Front wheel, 36 by 5 inches; cast steel; 8 U spokes; box rim. Weight—134 pounds. Chemical analysis (per cent)—Carbon, 0.19; sulphur, 0.081; phosphorus, 0.060; manganese, 0.74; silicon, 0.28]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 32 500 |
| Maximum applied load in pounds | 50 000 |
| Deformation at maximum load in inches | 0.0490 |
| Permanent set at maximum load in inches | 0.0135 |
| Slope of curve No. 2 in pounds per inch | 1 363 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 387 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 2.89 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 6 |
| 6000 pounds | 13 |
| 8000 pounds | 24 |
| 10 000 pounds | 37 |
| 12 000 pounds | 53 |
| 14 000 pounds | 72 |
| 16 000 pounds | 94 |
| 18 000 pounds | 119 |
| 20 000 pounds | 147 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 13 000 |
| Ultimate strength in pounds | 31 100 |
| Slope of curve at load in pounds per inch | 52 500 |
| Elastic resiliency in inch-pounds: | |
| At load | 1610 |
| 180° from load | 595 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 12.00 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 38 |
| 4000 pounds | 152 |
| 6000 pounds | 343 |
| 8000 pounds | 610 |
| 10 000 pounds | 954 |
| 12 000 pounds | 1371 |

Character of failure: Tension failure in spoke near point of application of load, and in webbing between spokes at 180° from load.

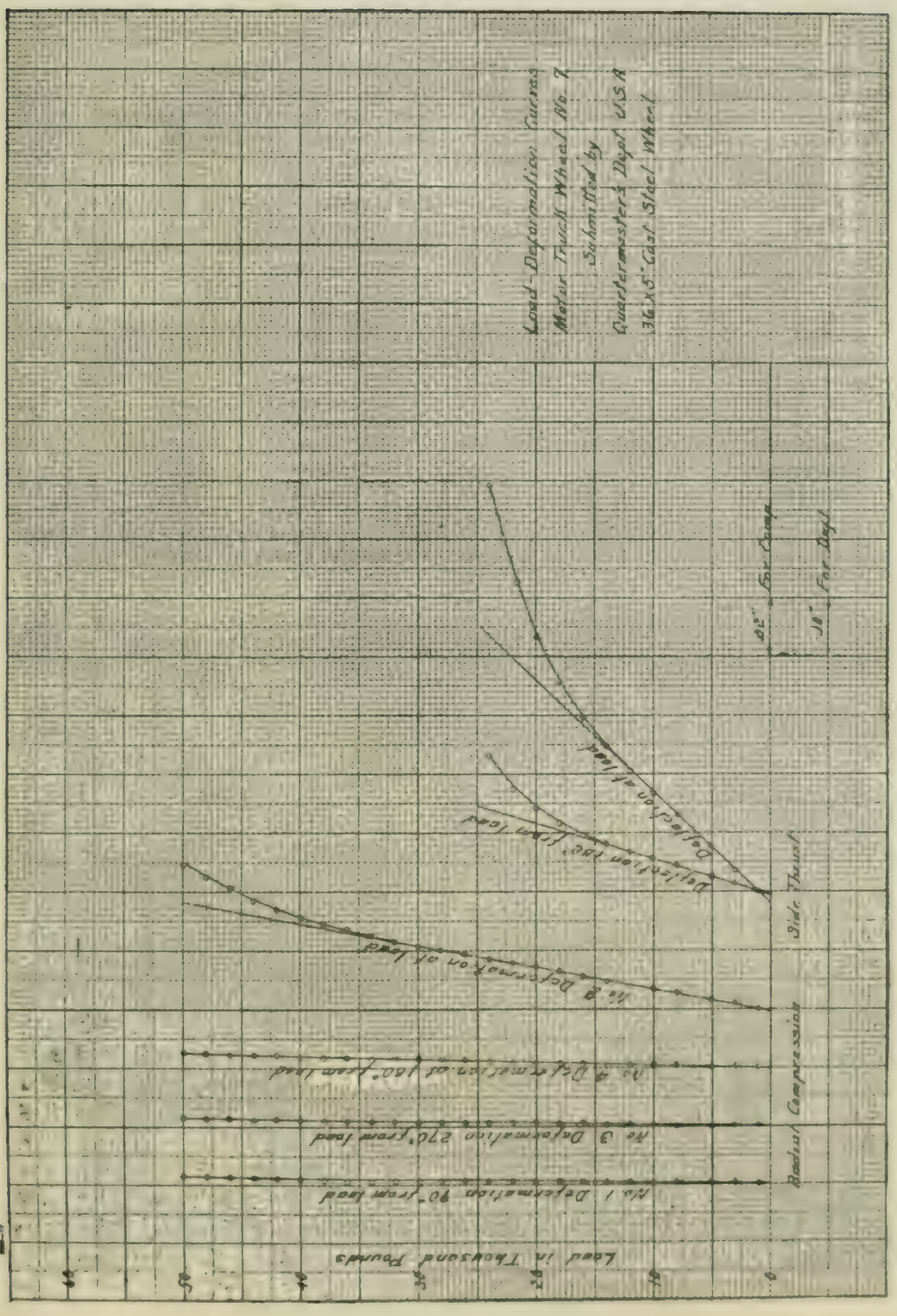


FIG. 14.—*Load-deformation curves, wheel No. 7*

## TABLE 15.—Wheel No. 8

[Description—Rear wheel, 36 by 10 inches; cast steel; 8 U spokes; box rim. Weight—274 pounds. Chemical analysis (per cent)—Carbon, 0.14; sulphur, 0.081; phosphorus, 0.080; manganese, 0.78; silicon, —]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 50 000 |
| Maximum applied load in pounds | 100 000 |
| Deformation at maximum load in inches | 0.0610 |
| Permanent set at maximum load in inches | 0.0103 |
| Slope of curve No. 2 in pounds per inch | 2 000 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 625 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 2.28 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 9 |
| 8000 pounds | 16 |
| 10 000 pounds | 25 |
| 12 000 pounds | 36 |
| 14 000 pounds | 49 |
| 16 000 pounds | 64 |
| 18 000 pounds | 81 |
| 20 000 pounds | 100 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 34 500 |
| Ultimate strength in pounds | 65 000 |
| Slope of curve at load in pounds per inch | 131 500 |
| Elastic resiliency in inch-pounds: | |
| At load | 4520 |
| 180° from load | 2880 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 16.50 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 15 |
| 4000 pounds | 61 |
| 6000 pounds | 137 |
| 8000 pounds | 243 |
| 10 000 pounds | 380 |
| 12 000 pounds | 548 |
| 14 000 pounds | 746 |
| 16 000 pounds | 973 |
| 18 000 pounds | 1232 |
| 20 000 pounds | 1521 |

Character of failure: Tension failure at root of spokes near point of application load and in webbing and web bracing 180° from load.

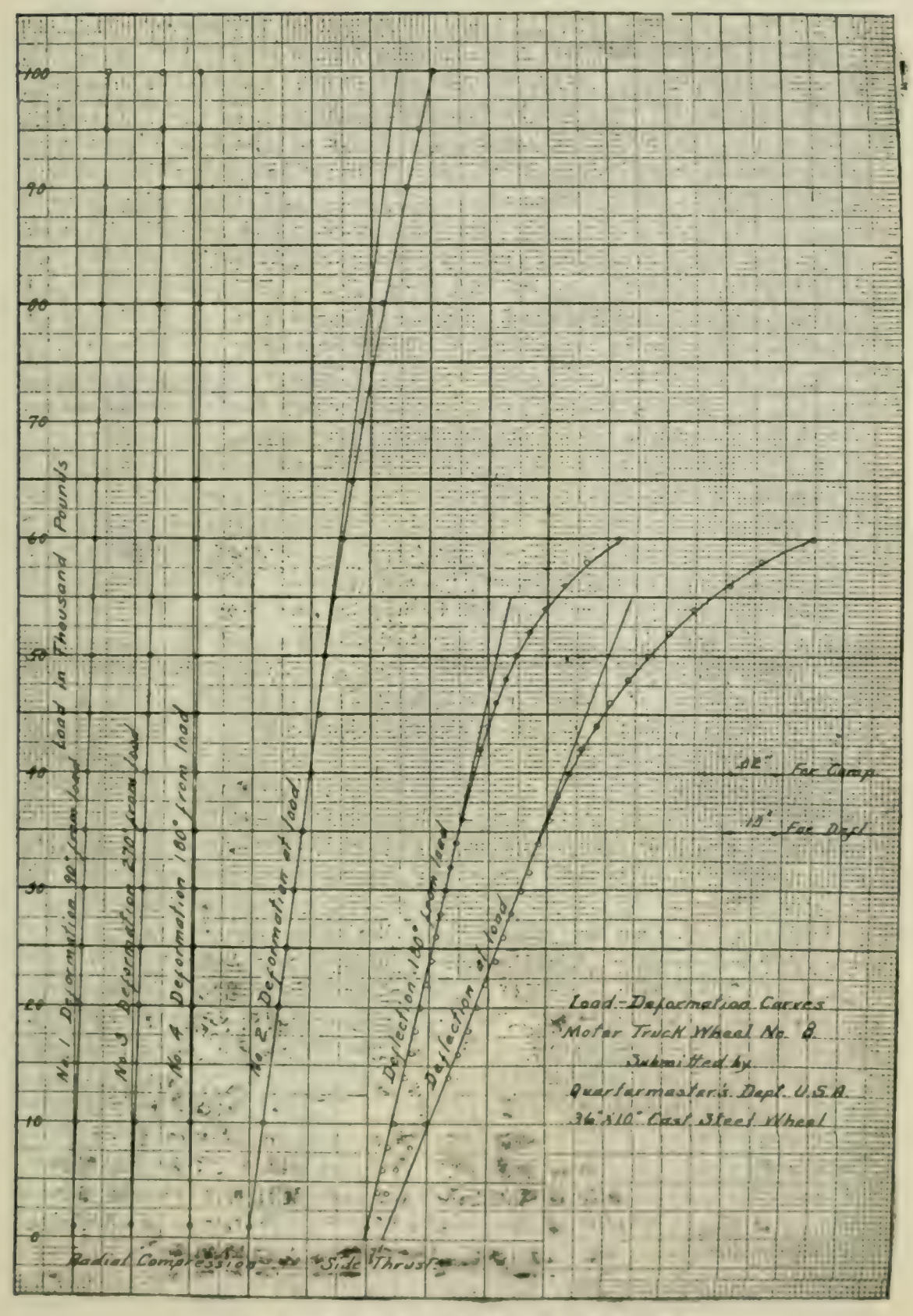


FIG. 15 —*Load-deformation curves, wheel No. 8*

## TABLE 16.—Wheel No. 9

[Description.—Front wheel, 36 by 5 inches; cast steel; 7 U spokes; box rim. Weight—136 pounds. Chemical analysis (per cent)—Carbon, 0.22; sulphur, 0.057; phosphorus, 0.038; manganese, 0.52; silicon, 0.266]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 35 500 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.1287 |
| Permanent set at maximum load in inches | 0.0791 |
| Slope of curve No. 2 in pounds per inch | 667 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | 119 |
| At load | 1047 |
| 270° from load | 150 |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load per pound of metal in wheel | 7.70 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 5 |
| 4000 pounds | 18 |
| 6000 pounds | 36 |
| 8000 pounds | 64 |
| 10 000 pounds | 95 |
| 12 000 pounds | 138 |
| 14 000 pounds | 182 |
| 16 000 pounds | 240 |
| 18 000 pounds | 297 |
| 20 000 pounds | 350 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 7500 |
| Ultimate strength in pounds | 26 700 |
| Slope of curve in pounds per inch | 36 400 |
| Elastic resiliency in inch-pounds: | |
| At load | 772 |
| 180° from load | 413 |
| Elastic resiliency in inch-pounds at load per pound of metal in wheel | 5.67 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 55 |
| 4000 pounds | 220 |
| 6000 pounds | 494 |
| 8000 pounds | 879 |

Character of failure: Tension failure in two spokes at load. One spoke failed near the rim and the other at the hub.

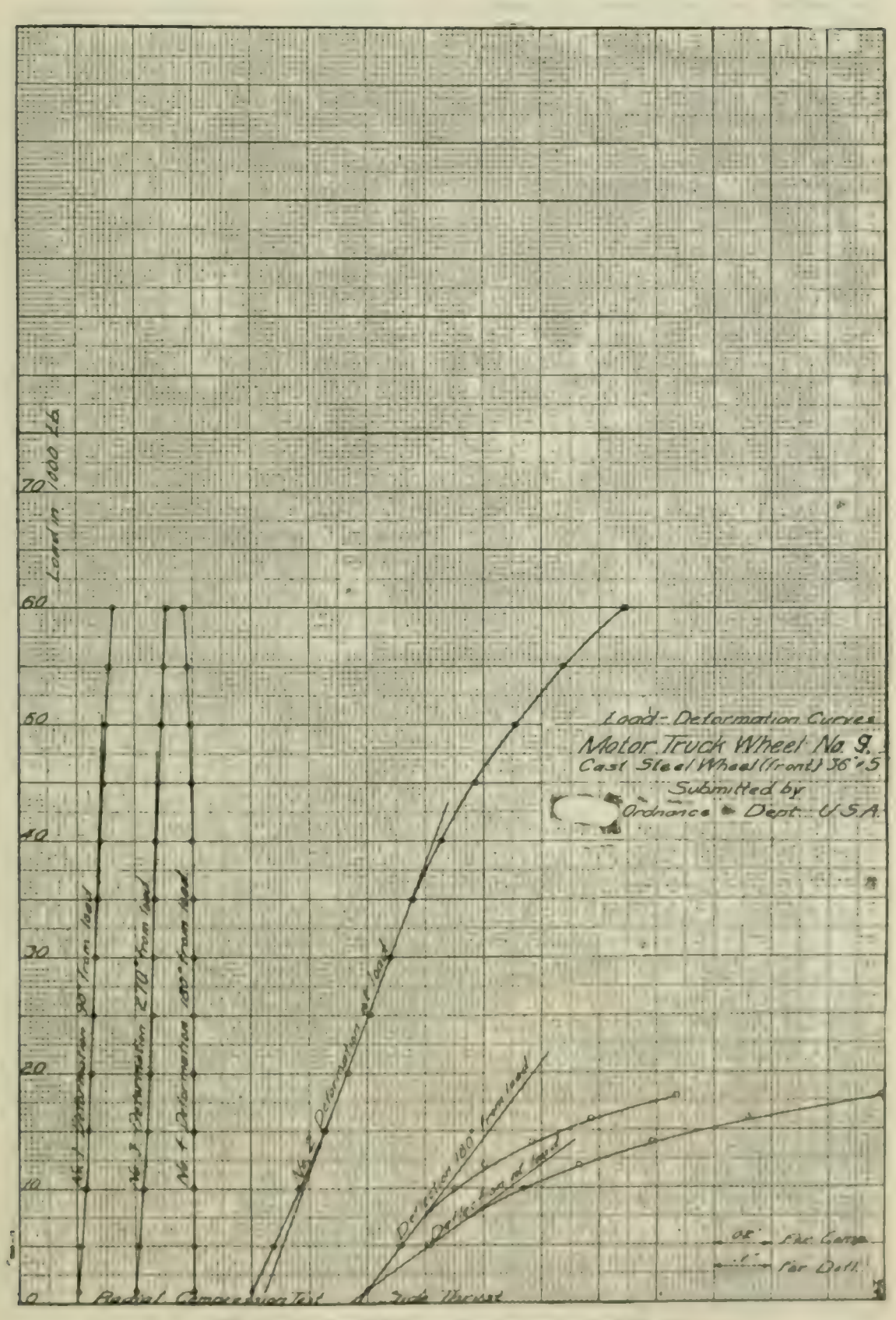


FIG. 16.—*Load-deformation curves, wheel No. 9*

## TABLE 17.—Wheel No. 10

[Description.—Rear wheel, 36 by 10 inches; cast steel; 7 U spokes; box rim. Weight—321 pounds. Chemical analysis (per cent)—Carbon, 0.23; sulphur, 0.061; phosphorus, 0.041; manganese, 0.62; silicon, 0.305]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 77 000 |
| Maximum applied load in pounds | 120 000 |
| Deformation at maximum load in inches | 0.1250 |
| Permanent set at maximum load in inches | 0.0537 |
| Slope of curve No. 2 in pounds per inch | 1 316 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 2250 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load per pound of metal in wheel | 7.00 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 5 |
| 4000 pounds | 17 |
| 6000 pounds | 39 |
| 8000 pounds | 64 |
| 10 000 pounds | 95 |
| 12 000 pounds | 132 |
| 14 000 pounds | 168 |
| 16 000 pounds | 208 |
| 18 000 pounds | 261 |
| 20 000 pounds | 310 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 35 000 |
| Ultimate strength in pounds | 81 700 |
| Slope of curve in pounds per inch | 125 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 5440 |
| 180° from load | 4100 |
| Elastic resiliency in inch-pounds at load per pound of metal in wheel | 16.9 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 20 |
| 4000 pounds | 86 |
| 6000 pounds | 180 |
| 8000 pounds | 320 |
| 10 000 pounds | 500 |
| 12 000 pounds | 720 |
| 14 000 pounds | 980 |
| 16 000 pounds | 1280 |
| 18 000 pounds | 1530 |
| 20 000 pounds | 1900 |

Character of failure: Tension failure at root of two spokes adjacent to the load.

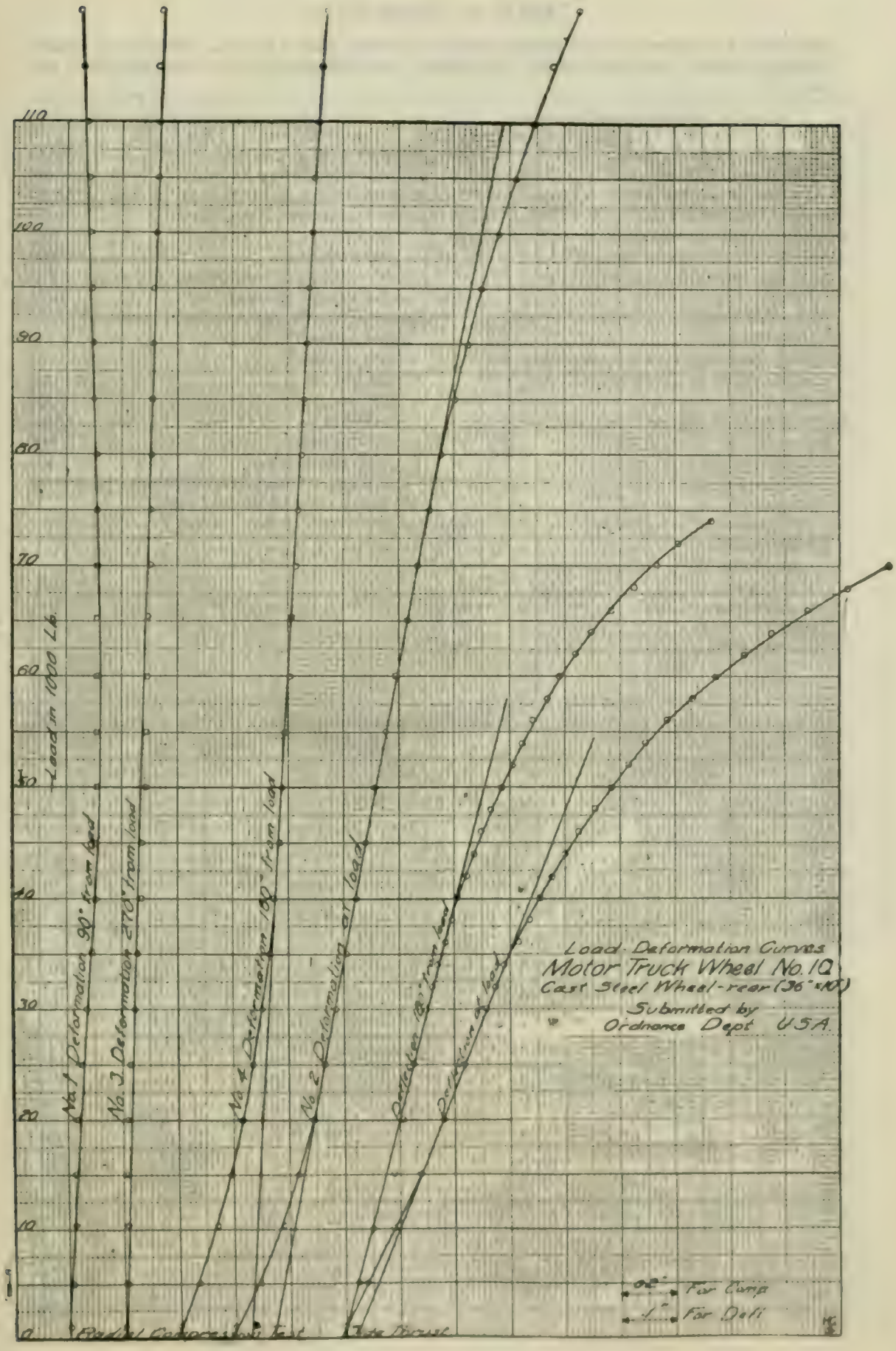
Load in 1000 Lb.
No. 1 Deformation 90° from load
No. 3 Deformation 270° from load
No. 4 Deformation 180° from load
No. 2 Deformation at load
Deflection 18" from load
Deflection at load
Load-Deformation Curves
Motor Truck Wheel No. 10
Cast Steel Wheel - rear (36" x 10")
Submitted by
Ordnance Dept U.S.A.
For Clamp
For Deflection

FIG. 17.—*Load-deformation curves, wheel No. 10*

## TABLE 18.—Wheel No. 11

Description—Front wheel, 36 by 5 inches; cast steel; 5 hollow spokes; box rim. **Weight—144 pounds.** Chemical analysis (per cent)—Carbon, 0.19; sulphur, 0.068; phosphorus, 0.040; manganese, 0.85; silicon, 0.23]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 32 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0695 |
| Permanent set at maximum load in inches | 0.0311 |
| Slope of curve No. 2 in pounds per inch | 1 160 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 441 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load per pound of metal in wheel | 3.06 |
| Resiliency in inch-pounds at point of appli-tion of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 7 |
| 6000 pounds | 16 |
| 8000 pounds | 28 |
| 10 000 pounds | 43 |
| 12 000 pounds | 62 |
| 14 000 pounds | 84 |
| 16 000 pounds | 110 |
| 18 000 pounds | 140 |
| 20 000 pounds | 173 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 13 000 |
| Ultimate strength in pounds | 39 300 |
| Slope of curve at load in pounds per inch | 58 100 |
| Elastic resiliency in inch-pounds: | |
| At load | 1460 |
| 180° from load | 1680 |
| Elastic resiliency in inch-pounds at load per pound of metal in wheel | 10.10 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 35 |
| 4000 pounds | 138 |
| 6000 pounds | 310 |
| 8000 pounds | 551 |
| 10 000 pounds | 860 |
| 12 000 pounds | 1235 |

Character of failure: Tension failure in hub at 180° from point of application of load.

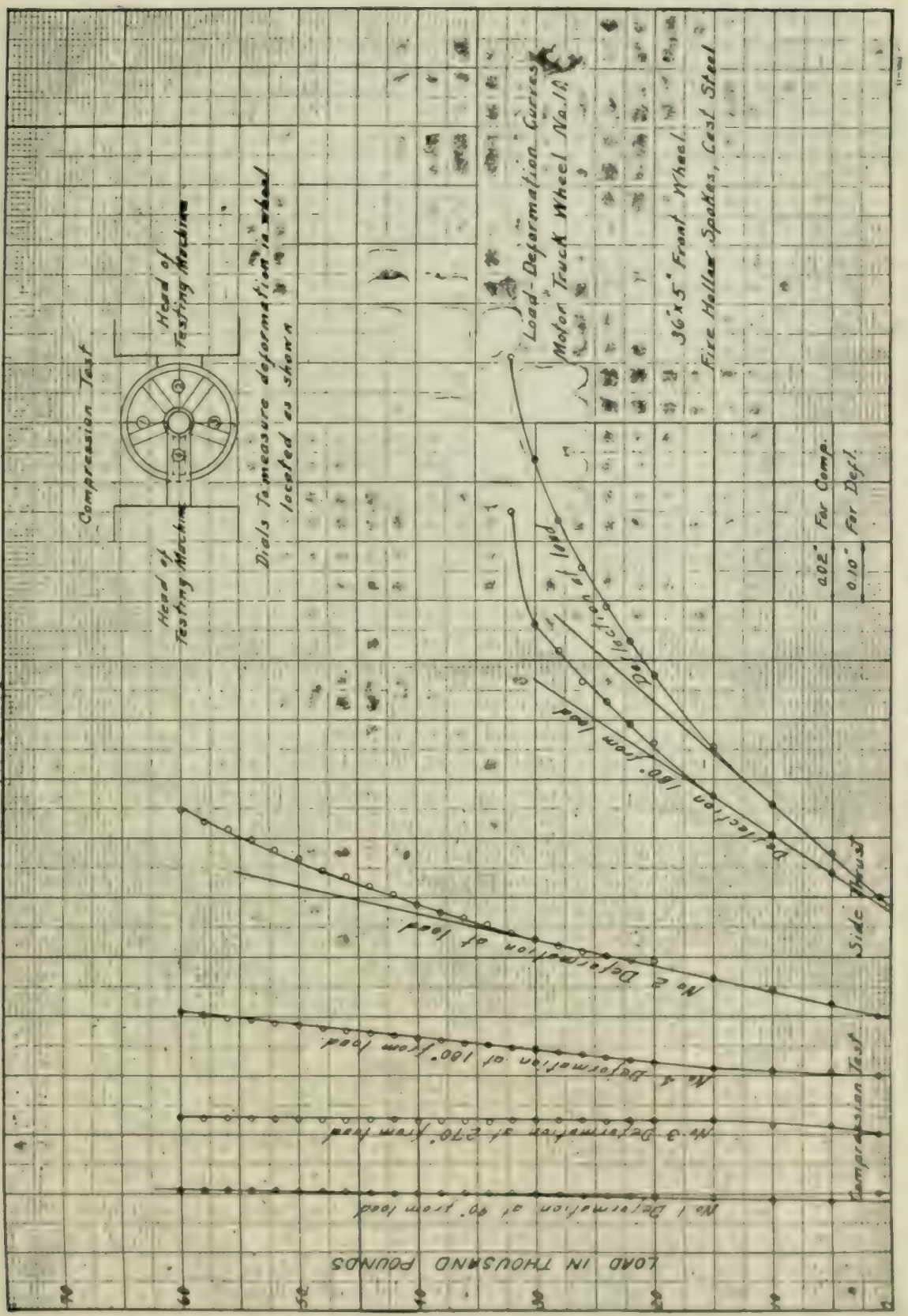
Load-Deformation Curves
Motor Truck Wheel No. 11
36"x5" Front Wheel.
Five Hollow Spokes, Cast Steel
Compression Test
Head of Testing Machine
Dials to measure deformation in wheel located as shown
Head of Testing Machine
.002" For Comp.
.010" For Defl.
Side Thrust
Compression Test
No. 1 Deformation at 90° from load
No. 3 Deformation at 270° from load
No. 4 Deformation at 180° from load
No. 2 Deformation at load
Deflection 180° from load
Deflection at load
LOAD IN THOUSAND POUNDS

FIG. 18.—*Load-deformation curves, wheel No. 11*

## TABLE 19.—Wheel No. 12

[Description—Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; box rim. Weight—130 pounds. Chemical analysis—Carbon, 0.307; sulphur, 0.043; phosphorus, 0.032; manganese, 0.75; silicon, 0.61]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 40 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0645 |
| Permanent set at maximum load in inches | 0.0220 |
| Slope of curve No. 2 in pounds per inch | 1 333 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 600 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 4.60 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 7 |
| 4000 pounds | 6 |
| 6000 pounds | 14 |
| 8000 pounds | 24 |
| 10 000 pounds | 38 |
| 12 000 pounds | 54 |
| 14 000 pounds | 74 |
| 16 000 pounds | 96 |
| 18 000 pounds | 122 |
| 20 000 pounds | 150 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 16 500 |
| Ultimate strength in pounds | 49 200 |
| Slope of curve in pounds per inch | 74 800 |
| Elastic resiliency in inch-pounds: | |
| At load | 1820 |
| 180° from load | 1480 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 14.0 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 27 |
| 4000 pounds | 107 |
| 6000 pounds | 241 |
| 8000 pounds | 428 |
| 10 000 pounds | 668 |
| 12 000 pounds | 963 |
| 14 000 pounds | 1310 |
| 16 000 pounds | 1710 |

Character of failure: Failed by buckling on the inside of the wheel near the point of application of load, in the metal at the base of the spokes near the solid metal hub.

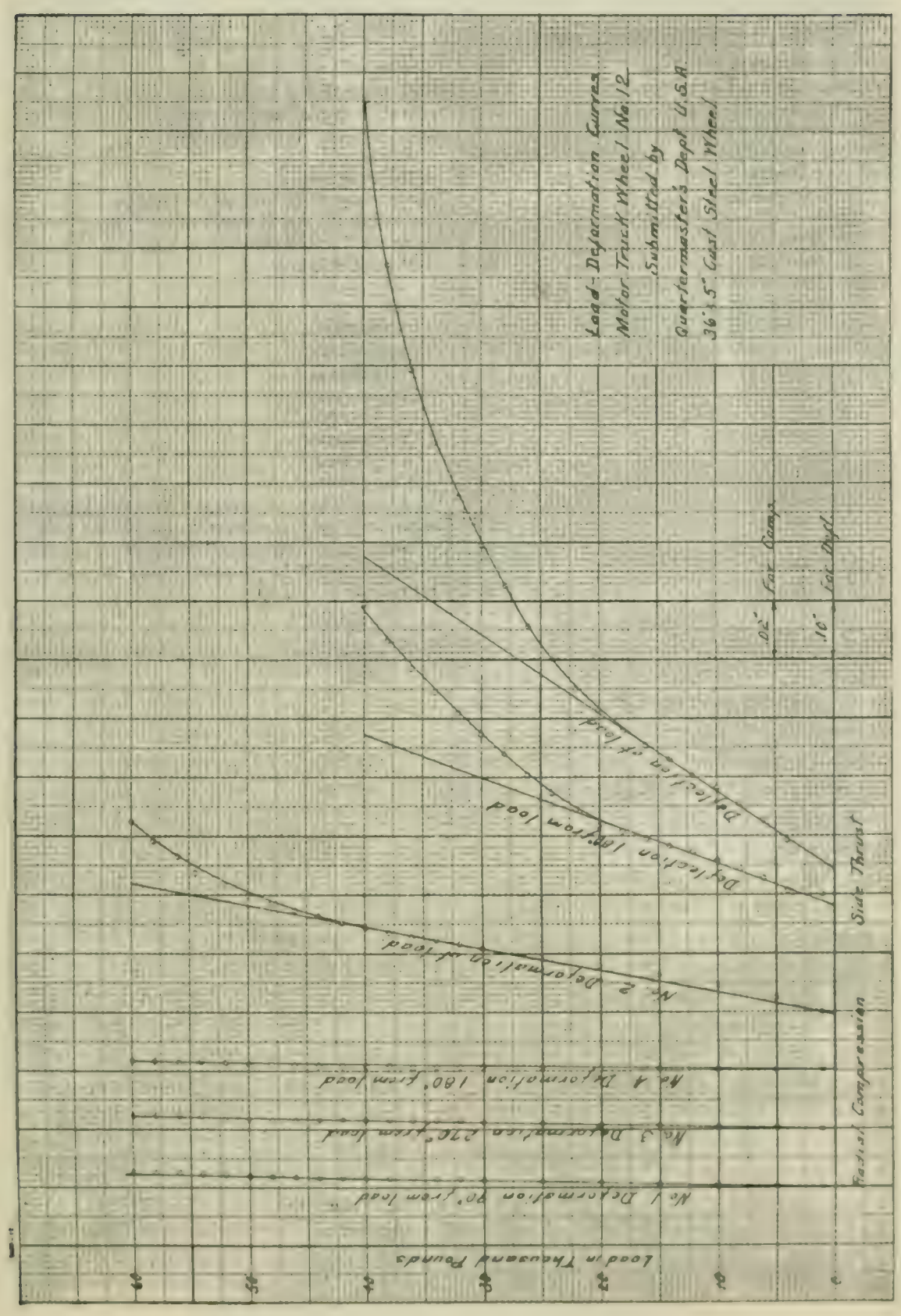
Load - Deformation Curves
Motor Truck Wheel No. 12
Submitted by
Quartermaster's Dept. U.S.A.
36 x 5" Cast Steel Wheel
.05" Tan Comp.
.10" Tan Appl.
Deflection at load
Deflection 180° from load
No. 2 Deformation at load
No. 4 Deformation 180° from load
No. 3 Deformation 270° from load
No. 1 Deformation 90° from load
Radial Compression
Side Thrust
Load in Thousand Pounds

FIG. 19.—*Load-deformation curves, wheel No. 12*

## TABLE 20.—Wheel No. 13

[Description—Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; box rim. Weight—286 pounds. Chemical analysis (per cent)—Carbon, 0.362; sulphur, 0.043; phosphorus, 0.038; manganese, 0.76; silicon, 0.54]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 20 000 |
| Maximum applied load in pounds | 100 000 |
| Deformation at maximum load in inches | 0.0513 |
| Permanent set at maximum load in inches | 0.0113 |
| Slope of curve No. 2 in pounds per inch | 6 060 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 33 |
| 270° from load | |
| 180° from load | 390 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 0.10 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 0 |
| 4000 pounds | 1 |
| 6000 pounds | 3 |
| 8000 pounds | 5 |
| 10 000 pounds | 8 |
| 12 000 pounds | 12 |
| 14 000 pounds | 16 |
| 16 000 pounds | 21 |
| 18 000 pounds | 27 |
| 20 000 pounds | 33 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 38 000 |
| Ultimate strength in pounds | 101 000 |
| Slope of cruve in pounds per inch | 179 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 4040 |
| 180° from load | 5170 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 14.20 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 11 |
| 4000 pounds | 45 |
| 6000 pounds | 105 |
| 8000 pounds | 179 |
| 10 000 pounds | 279 |
| 12 000 pounds | 402 |
| 14 000 pounds | 547 |
| 16 000 pounds | 714 |
| 18 000 pounds | 903 |
| 20 000 pounds | 1116 |

Character of failure: Apparatus broke at 101 000 pounds, making it necessary to remove the load. On reapplying load, the wheel failed at 98 000 pounds by tension fraction in the steel where the spokes join the hub.

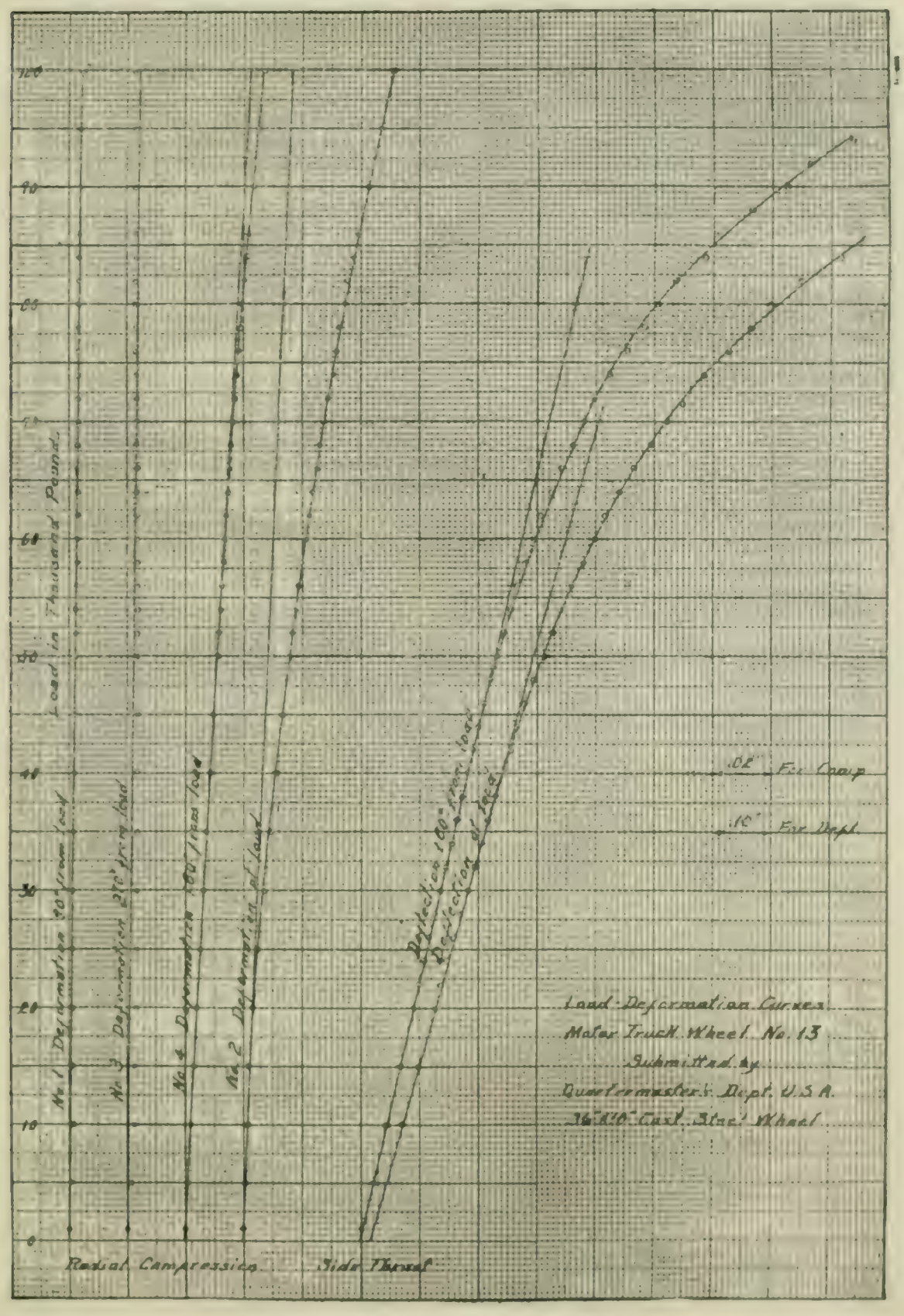


FIG. 20.—*Load-deformation curves, wheel No. 13*

## TABLE 21.—Wheel No. 14

[Description—Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; composite design. Weight—132 pounds. Chemical analysis (per cent)—Carbon, 0.30; sulphur, 0.034; phosphorus, 0.021; manganese, 0.47; silicon, 0.40]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 26 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.1135 |
| Permanent set at maximum load in inches | 0.0687 |
| Slope of cruve No. 2 in pounds per inch | 1 300 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 260 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 1.97 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 5 |
| 6000 pounds | 14 |
| 8000 pounds | 25 |
| 10 000 pounds | 39 |
| 12 000 pounds | 55 |
| 14 000 pounds | 75 |
| 16 000 pounds | 98 |
| 18 000 pounds | 125 |
| 20 000 pounds | 154 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 10 500 |
| Ultimate strength in pounds | 34 000 |
| Slope of cruve in pounds per inch | 63 700 |
| Elastic resiliency in inch-pounds: | |
| At load | 865 |
| 180° from load | 330 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 6.55 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 31 |
| 4000 pounds | 126 |
| 6000 pounds | 282 |
| 8000 pounds | 502 |
| 10 000 pounds | 785 |

**Character of failure: Failed by the crushing in of one side of tire seat at point of application of load, and by distortion of wheel. There were no signs of rupture in the metal.**

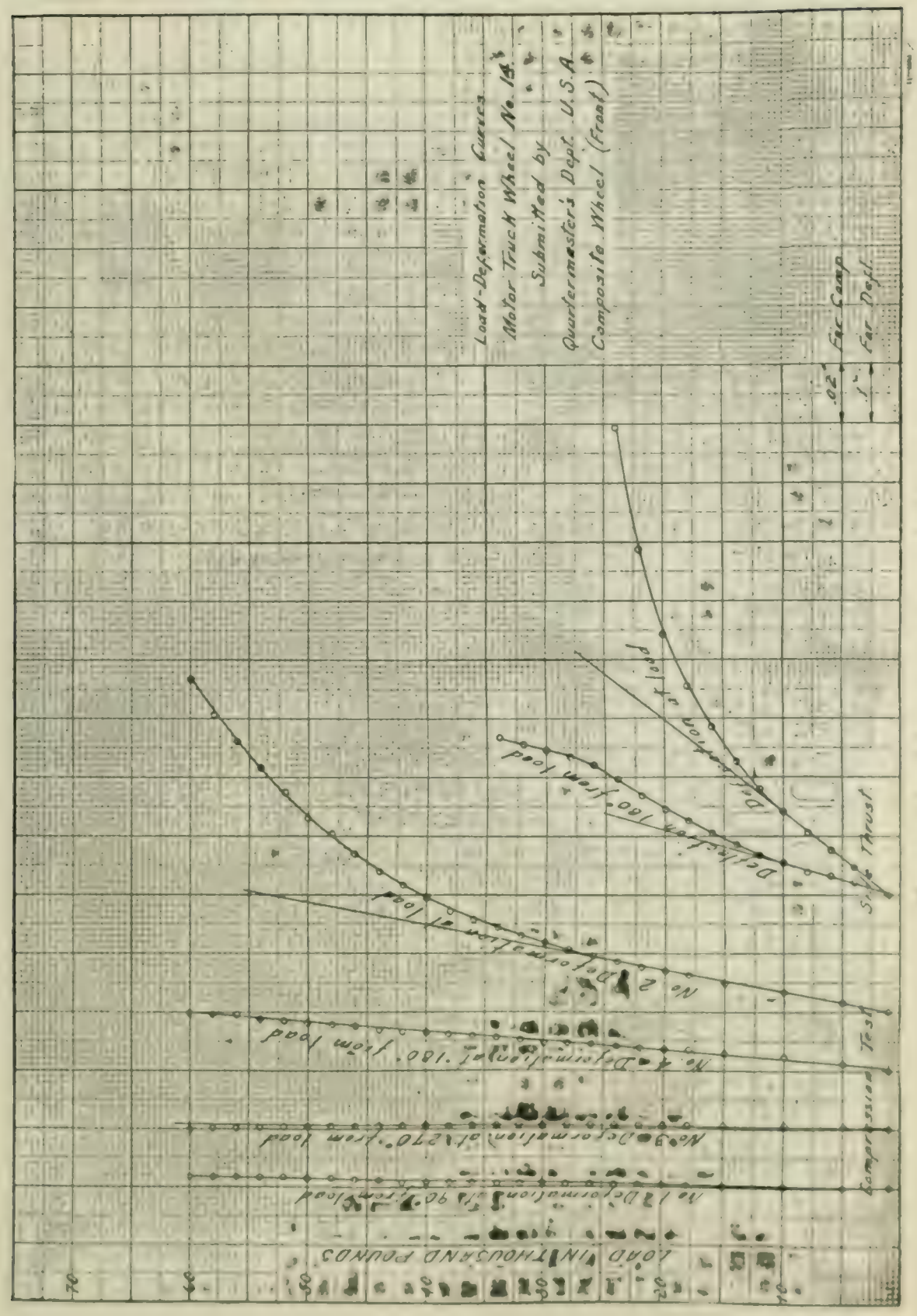


FIG. 21.—*Load-deformation curves, wheel No. 14*

## TABLE 22.—Wheel No. 15

[Description—Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; composite design. Weight—249 pounds. Chemical analysis (per cent)—Carbon, 0.40; sulphur, 0.038; phosphorus, 0.021; manganese, 0.69; silicon, 0.46]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 75 000 |
| Maximum applied load in pounds | 120 000 |
| Deformation at maximum load in inches | 0.0874 |
| Permanent set at maximum load in inches | 0.0318 |
| Slope of curve No. 2 in pounds per inch | 2 320 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 1210 |
| 270° from load | |
| 180° from load | 880 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 4.86 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 8 |
| 8000 pounds | 14 |
| 10 000 pounds | 22 |
| 12 000 pounds | 31 |
| 14 000 pounds | 42 |
| 16 000 pounds | 55 |
| 18 000 pounds | 70 |
| 20 000 pounds | 86 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limi in pounds | 37 500 |
| Ultimate strength in pounds | 68 000 |
| Slope of curve in pounds per inch | 107 100 |
| Elastic resiliency in inch-pounds: | |
| At load | 6550 |
| 180° from load | 6480 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 26.3 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 19 |
| 4000 pounds | 75 |
| 6000 pounds | 168 |
| 8000 pounds | 299 |
| 10 000 pounds | 468 |
| 12 000 pounds | 672 |
| 14 000 pounds | 914 |
| 16 000 pounds | 1195 |
| 18 000 pounds | 1512 |
| 20 000 pounds | 1866 |

Character of failure: Failed by crushing in of tire seat at point of application of load.

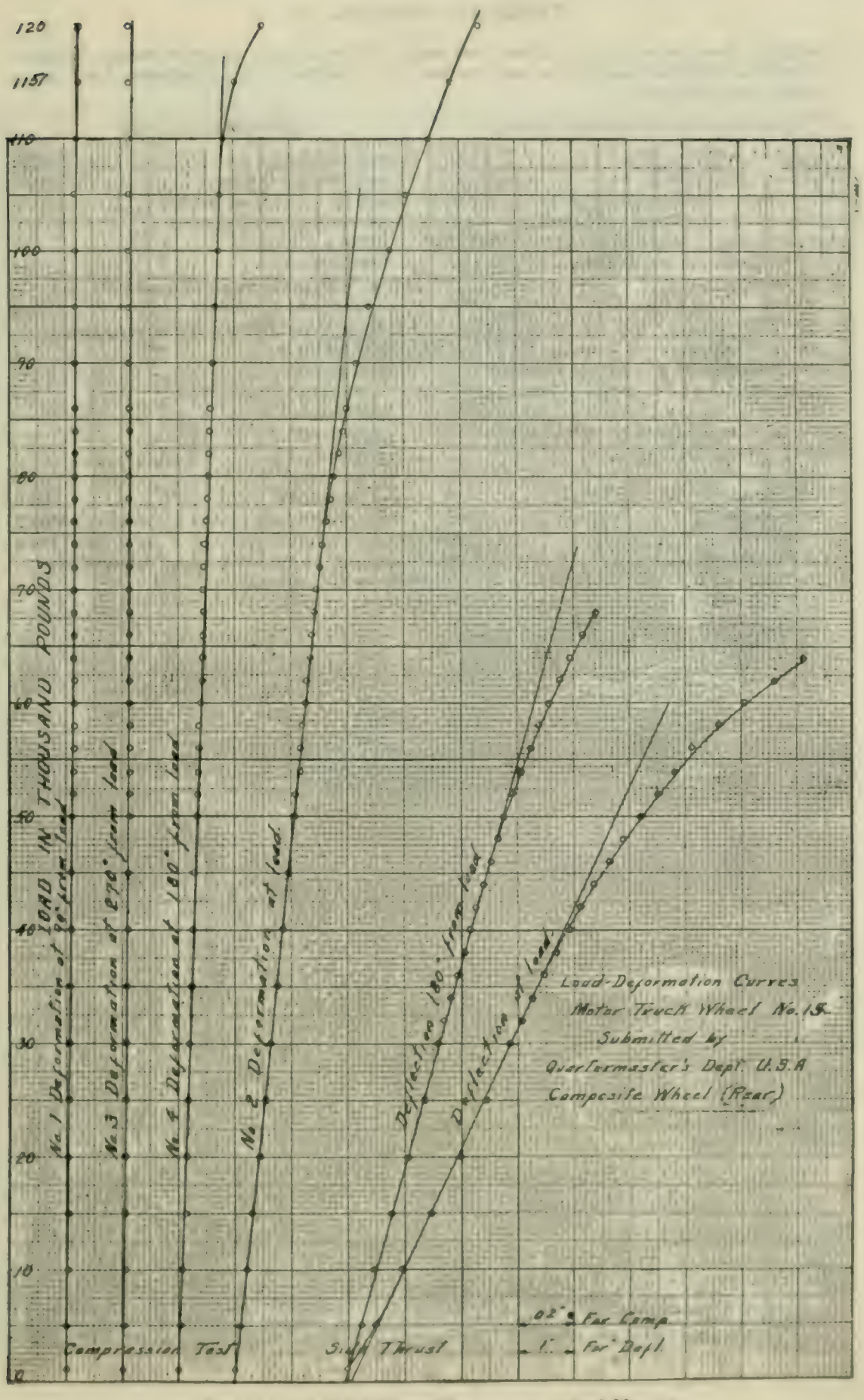


FIG. 22.—*Load-deformation curves, wheel No. 15*

## TABLE 23.—Wheel No. 16

[Description - Front wheel, 36 by 5 inches; cast steel; 7 hollow spokes; composite design. Weight—120 pounds. Chemical analysis (per cent)—Carbon, 0.211; sulphur, 0.082; phosphorus, 0.066; manganese, 0.84; silicon, 0.40]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 44 000 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0744 |
| Permanent set at maximum load in inches | 0.0323 |
| Slope of curve No. 2 in pounds per inch | 917 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | .... |
| At load | 1056 |
| 270° from load | .... |
| 180° from load | .... |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 8.80 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 9 |
| 6000 pounds | 20 |
| 8000 pounds | 35 |
| 10 000 pounds | 55 |
| 12 000 pounds | 79 |
| 14 000 pounds | 107 |
| 16 000 pounds | 140 |
| 18 000 pounds | 177 |
| 20 000 pounds | 218 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 14 000 |
| Ultimate strength in pounds | 30 200 |
| Slope of curve in pounds per inch | 43 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 2280 |
| 180° from load | 700 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 19.00 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 47 |
| 4000 pounds | 186 |
| 6000 pounds | 418 |
| 8000 pounds | 744 |
| 10 000 pounds | 1160 |
| 12 000 pounds | 1675 |
| 14 000 pounds | 2280 |

Character of failure: Failed by spokes tearing from hub near point of application of load. This wheel was a poor casting, and cracks developed due to flaws in the material.

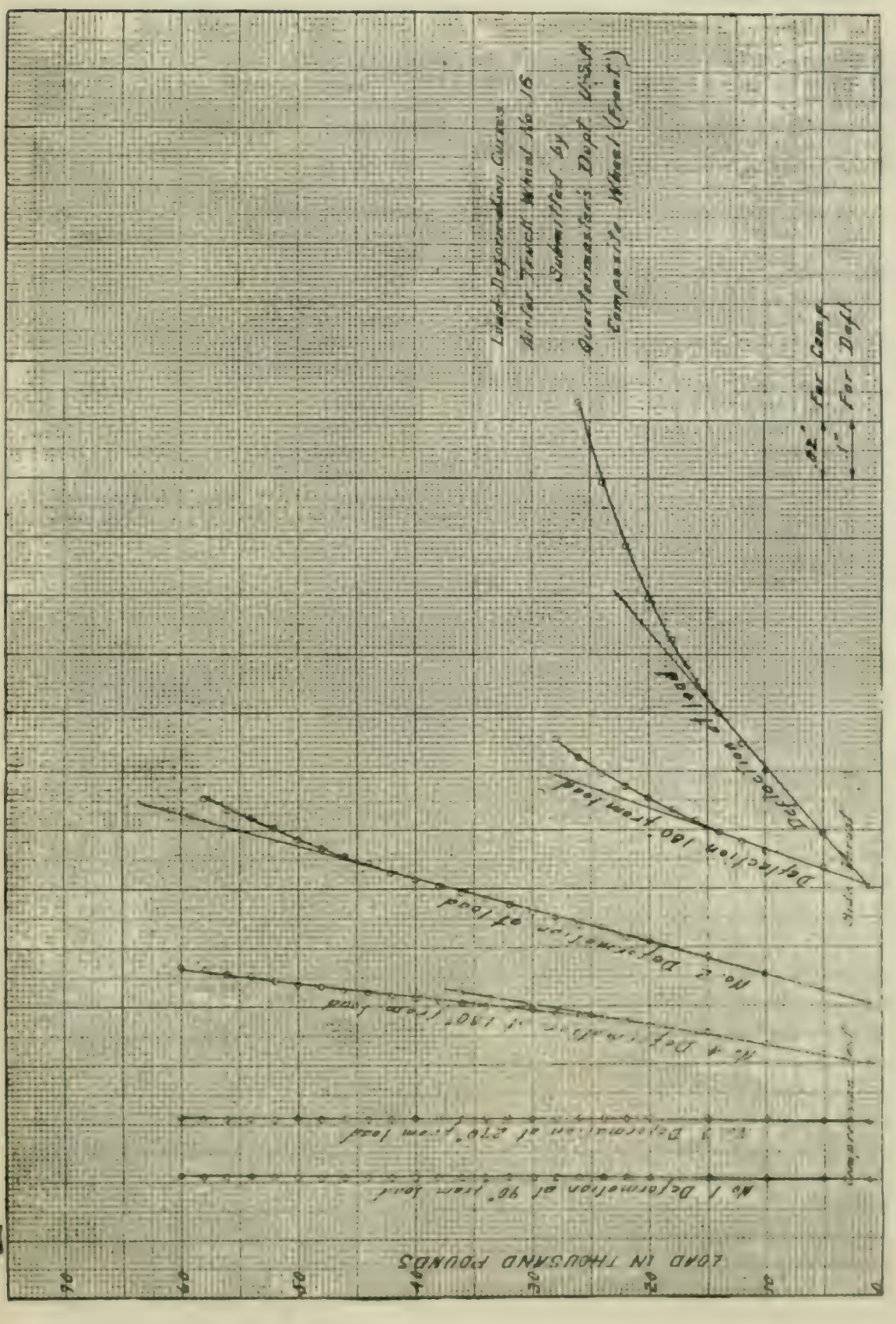
Load-Deformation Curves
Relief Truck Wheel No. 16
Submitted by
Quartermaster's Dept. U.S.A.
Timpanized Wheel (Front)
12" Car Comp
1" Car Dept
Load in Thousand Pounds
No. 1 Deformation at 90° from load
No. 3 Deformation at 210° from load
No. 4 Deformation at 150° from load
No. 2 Deformation at load
Deflection 180° from load
Deflection load at load

FIG. 23.—*Load-deformation curves, wheel No. 16*

## TABLE 24.—Wheel No. 17

Description—Rear wheel, 36 by 10 inches; cast steel; 7 hollow spokes; composite design. Weight—273 pounds. Chemical analysis (per cent)—Carbon, 0.19; sulphur, 0.084; phosphorus, 0.070; manganese, 0.79; silicon, 0.23]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 71 500 |
| Maximum applied load in pounds | 120 000 |
| Deformation at maximum load in inches | 0.1586 |
| Permanent set at maximum load in inches | 0.0831 |
| Slope of curve No. 2 in pounds per inch | 1 250 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | 640 |
| At load | 2090 |
| 270° from load | 630 |
| 180° from load | 319 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 7.65 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 2 |
| 4000 pounds | 6 |
| 6000 pounds | 14 |
| 8000 pounds | 26 |
| 10 000 pounds | 40 |
| 12 000 pounds | 58 |
| 14 000 pounds | 78 |
| 16 000 pounds | 102 |
| 18 000 pounds | 130 |
| 20 000 pounds | 160 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 40 000 |
| Ultimate strength in pounds | 60 600 |
| Slope of curve in pounds per inch | 104 000 |
| Elastic resiliency in inch-pounds: | |
| At load | 7 680 |
| 180° from load | 850 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 28.30 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 19 |
| 4000 pounds | 77 |
| 6000 pounds | 173 |
| 8000 pounds | 308 |
| 10 000 pounds | 481 |
| 12 000 pounds | 693 |
| 14 000 pounds | 943 |
| 16 000 pounds | 1232 |
| 18 000 pounds | 1558 |
| 20 000 pounds | 1924 |

Character of failure: Failed in hub near root of spokes at point of application of load. Poor casting.

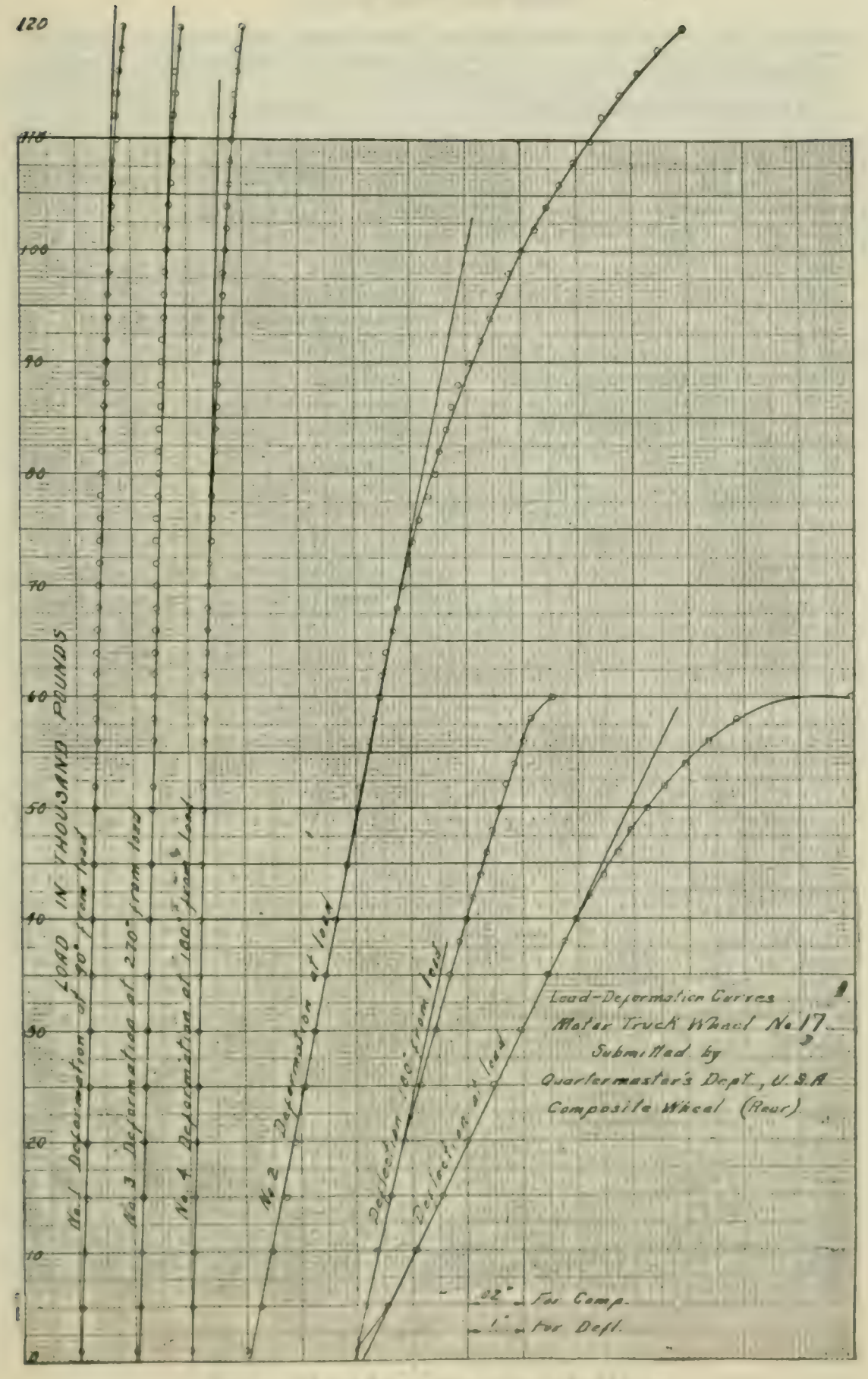


FIG. 24.—*Load-deformation curves, wheel No. 17*

## TABLE 25.—Wheel No. 18

[Description—Rear wheel, 40 by 10 inches; cast steel; 7 hollow spokes; composite design. Weight—325 pounds. Chemical analysis (per cent)—Carbon, 0.33; sulphur, 0.058; phosphorus, 0.033; manganese, 0.72; silicon, 0.43]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 45 000 |
| Maximum applied load in pounds | 120 000 |
| Deformation at maximum load in inches | 0.1230 |
| Permanent set at maximum load in inches | 0.0676 |
| Slope of curve No. 2 in pounds per inch | 1 968 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 538 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 1.66 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 9 |
| 8000 pounds | 16 |
| 10 000 pounds | 26 |
| 12 000 pounds | 37 |
| 14 000 pounds | 50 |
| 16 000 pounds | 65 |
| 18 000 pounds | 82 |
| 20 000 pounds | 102 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 35 000 |
| Ultimate strength in pounds | 82 300 |
| Slope of curve in pounds per inch | 93 200 |
| Elastic resiliency in inch-pounds: | |
| At load | 6560 |
| 180° from load | 4900 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 20.20 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 21 |
| 4000 pounds | 86 |
| 6000 pounds | 193 |
| 8000 pounds | 343 |
| 10 000 pounds | 536 |
| 12 000 pounds | 772 |
| 14 000 pounds | 1050 |
| 16 000 pounds | 1374 |
| 18 000 pounds | 1740 |
| 20 000 pounds | 2146 |

Character of failure: Tension failure in hub near point of application of load.

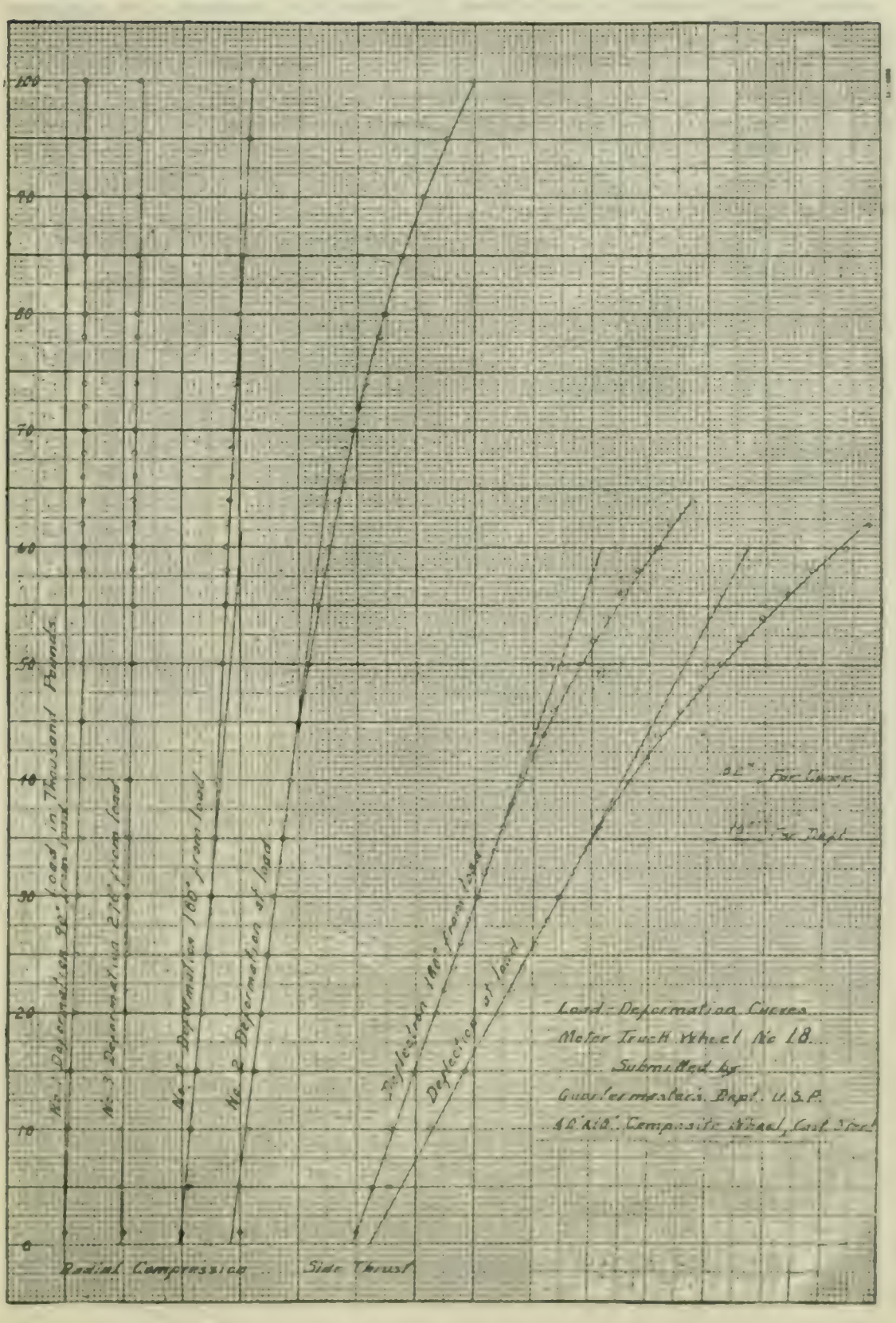


FIG. 25.—*Load-deformation curves, wheel No. 18*

## TABLE 26.—Wheel No. 19

[Description—Rear wheel, 40 by 12 inches; cast steel; 7 hollow spokes; composite design. Weight—325 pounds. Chemical analysis (per cent)—Carbon, 0.19; sulphur, 0.050; phosphorus, 0.048; manganese 0.36; silicon, 0.33]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 40 000 |
| Maximum applied load in pounds | 100 000 |
| Deformation at maximum load in inches | 0.1555 |
| Permanent set at maximum load in inches | 0.1100 |
| Slope of curve No. 2 in pounds per inch | 1 836 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | 195 |
| At load | 436 |
| 270° from load | 94 |
| 180° from load | 0 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 1.34 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 10 |
| 8000 pounds | 17 |
| 10 000 pounds | 27 |
| 12 000 pounds | 39 |
| 14 000 pounds | 53 |
| 16 000 pounds | 70 |
| 18 000 pounds | 88 |
| 20 000 pounds | 109 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 31 000 |
| Ultimate strength in pounds | 59 300 |
| Slope of curve in pounds per inch | 67 100 |
| Elastic resiliency in inch-pounds: | |
| At load | 7150 |
| 180° from load | 7700 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 22.00 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 30 |
| 4000 pounds | 119 |
| 6000 pounds | 269 |
| 8000 pounds | 477 |
| 10 000 pounds | 745 |
| 12 000 pounds | 1073 |
| 14 000 pounds | 1460 |
| 16 000 pounds | 1906 |
| 18 000 pounds | 2413 |
| 20 000 pounds | 2975 |

Character of failure: Tension failure in hub near point of application of load. Flaw in casting at point of failure.

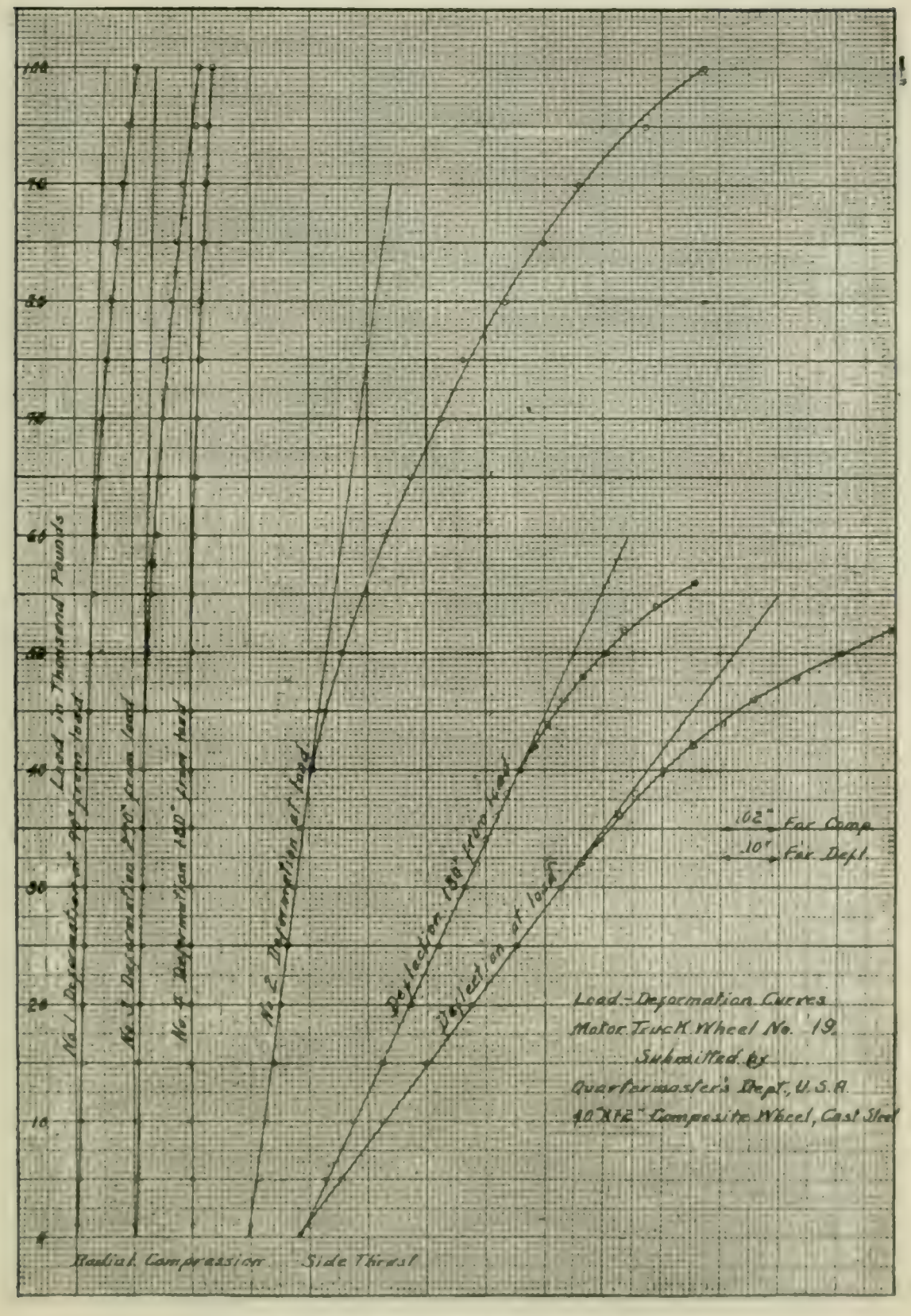


FIG. 26.—*Load-deformation curves, wheel No. 19*

## TABLE 27.—Wheel No. 20

[Description—Front wheel, 36 by 5 inches; malleable iron; 7 hollow spokes; composite design. Weight—141 pounds. Chemical analysis (per cent)—Carbon, 2.58; sulphur, 0.056; phosphorus, 0.199; manganese 0.21; silicon, 0.722]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 43 500 |
| Maximum applied load in pounds | 60 000 |
| Deformation at maximum load in inches | 0.0741 |
| Permanent set at maximum load in inches | 0.0271 |
| Slope of curve No. 2 in pounds per inch | 926 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | |
| At load | 1131 |
| 270° from load | |
| 180° from load | |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 8.02 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 4 |
| 4000 pounds | 16 |
| 6000 pounds | 33 |
| 8000 pounds | 56 |
| 10 000 pounds | 80 |
| 12 000 pounds | 108 |
| 14 000 pounds | 140 |
| 16 000 pounds | 176 |
| 18 000 pounds | 221 |
| 20 000 pounds | 270 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 12 500 |
| Ultimate strength in pounds | 25 300 |
| Slope of curve in pounds per inch | 45 400 |
| Elastic resiliency in inch-pounds: | |
| At load | 1718 |
| 180° from load | 310 |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 12.20 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 44 |
| 4000 pounds | 176 |
| 6000 pounds | 396 |
| 8000 pounds | 705 |
| 10 000 pounds | 1100 |
| 12 000 pounds | 1584 |

Character of failure: Tension failure in hub at root of the two spokes under the load.

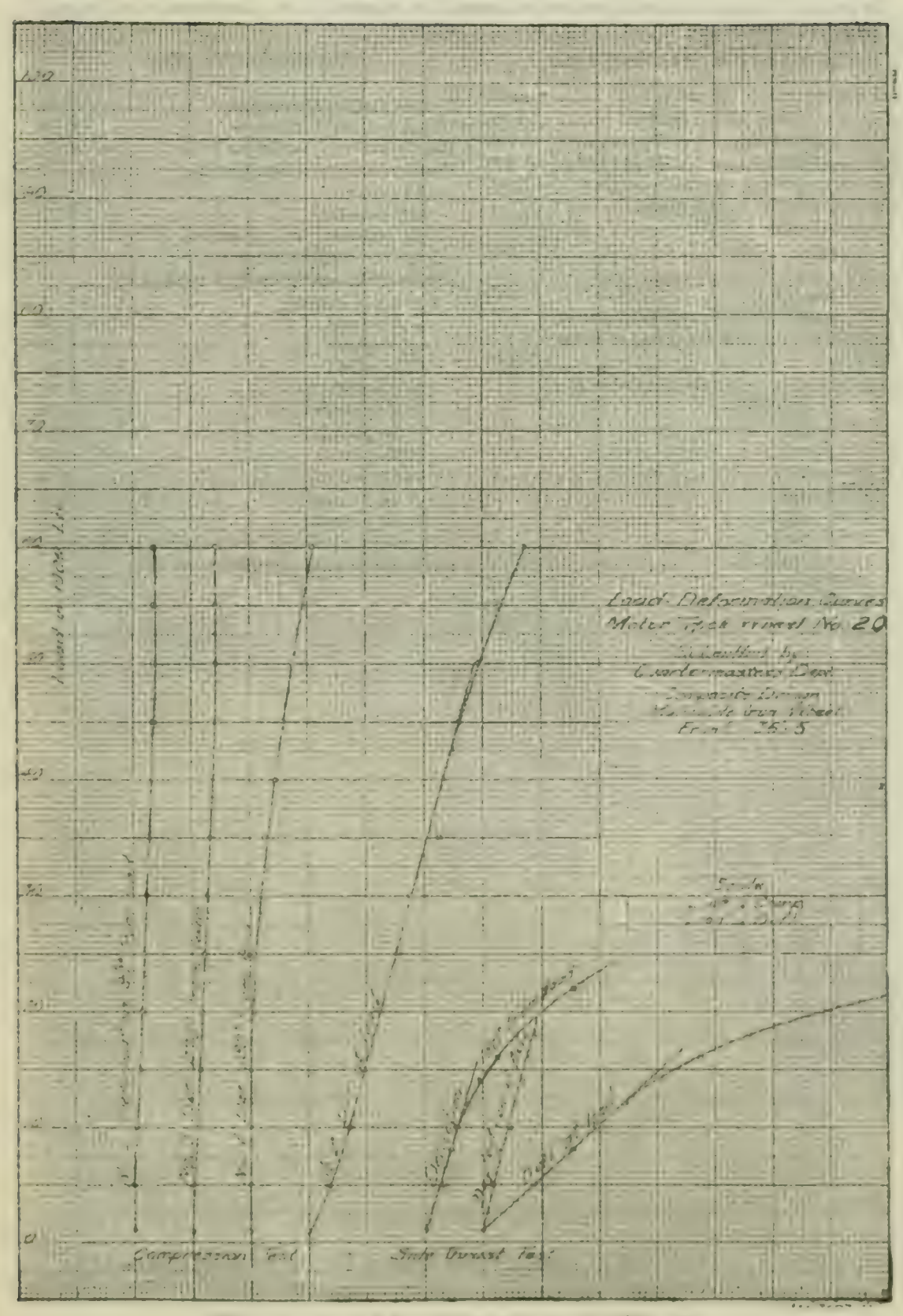


FIG. 27.—*Load-deformation curves, wheel No. 20*

## TABLE 28.—Wheel No. 21

[Description—Rear wheel, 40 by 10 inches; malleable iron; 7 hollow spokes; composite design. Weight—288 pounds. Chemical analysis (per cent)—Carbon, 2.39; sulphur, 0.078; phosphorus, 0.199; manganese, 0.23; silicon, 0.980]

### RADIAL-COMPRESSION TEST

| | |
|---|---|
| Proportional limit in pounds | 64 000 |
| Maximum applied load in pounds | 120 000 |
| Deformation at maximum load in inches | 0.1361 |
| Permanent set at maximum load in inches | 0.0715 |
| Slope of curve No. 2, in pounds per inch | 1 818 000 |
| Elastic resiliencies in inch-pounds: | |
| 90° from load | ..... |
| At load | 1128 |
| 270° from load | 255 |
| 180° from load | 450 |
| Elastic resiliencies in inch-pounds at point of application of load, per pound of metal in wheel | 3.91 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 1 |
| 4000 pounds | 4 |
| 6000 pounds | 10 |
| 8000 pounds | 18 |
| 10 000 pounds | 28 |
| 12 000 pounds | 40 |
| 14 000 pounds | 54 |
| 16 000 pounds | 70 |
| 18 000 pounds | 89 |
| 20 000 pounds | 110 |

### SIDE-THRUST TEST

| | |
|---|---|
| Proportional limit in pounds | 28 000 |
| Ultimate strength in pounds | 55 400 |
| Slope of curve in pounds per inch | 69 600 |
| Elastic resiliency in inch-pounds: | |
| At load | 7280 |
| 180° from load | ..... |
| Elastic resiliency in inch-pounds at load, per pound of metal in wheel | 25.30 |
| Resiliency in inch-pounds at point of application of load at— | |
| 2000 pounds | 70 |
| 4000 pounds | 270 |
| 6000 pounds | 555 |
| 8000 pounds | 900 |
| 10 000 pounds | 1300 |
| 12 000 pounds | 1740 |
| 14 000 pounds | 2240 |
| 16 000 pounds | 2760 |
| 18 000 pounds | 3380 |
| 20 000 pounds | 4000 |

Character of failure: Tension failure in two spokes and in rim at point of application of load

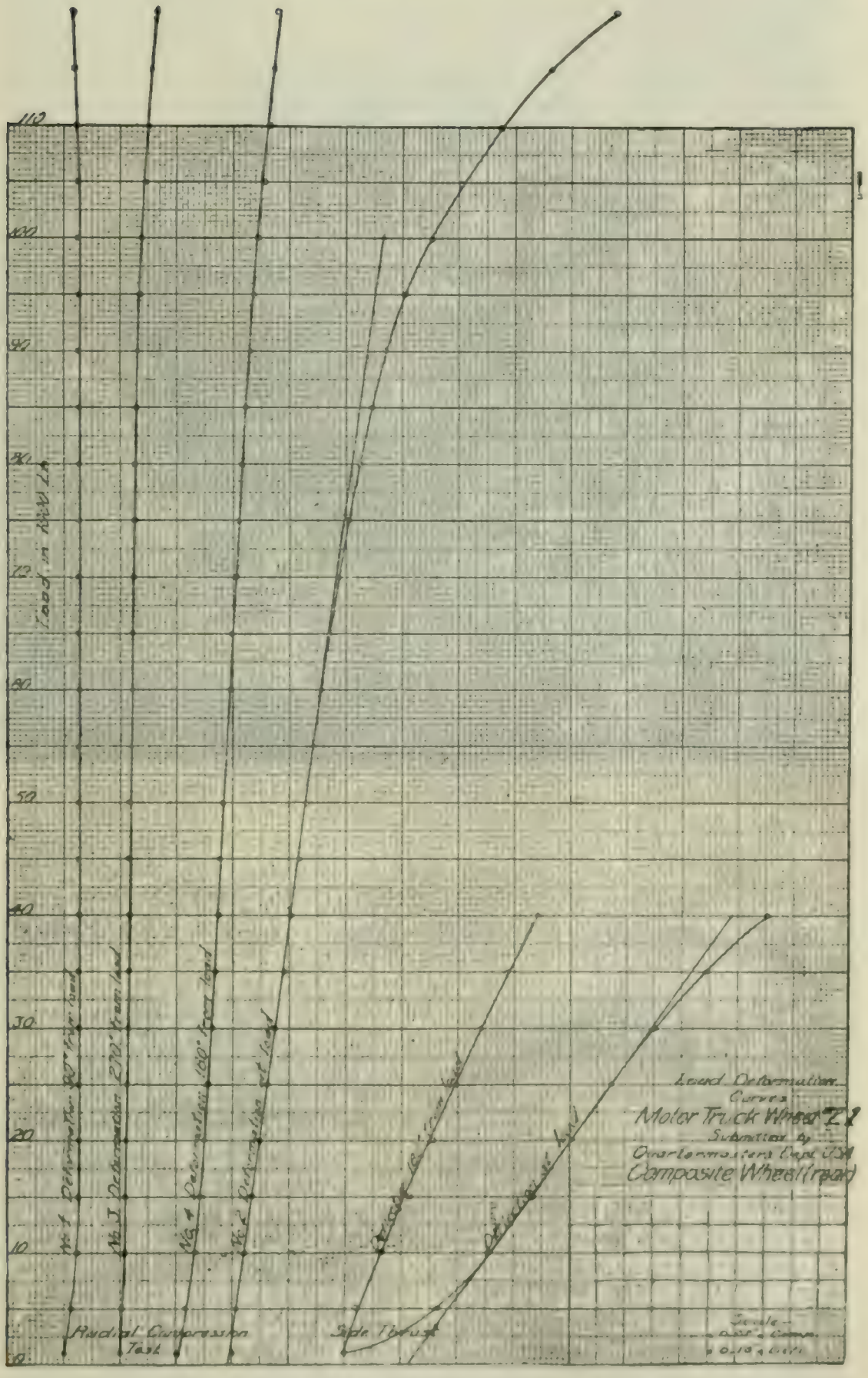


FIG. 28.—*Load-deformation curves, wheel No. 21*

WASHINGTON, July 11, 1919.

FIG. 29.—*Wheel No. 1*

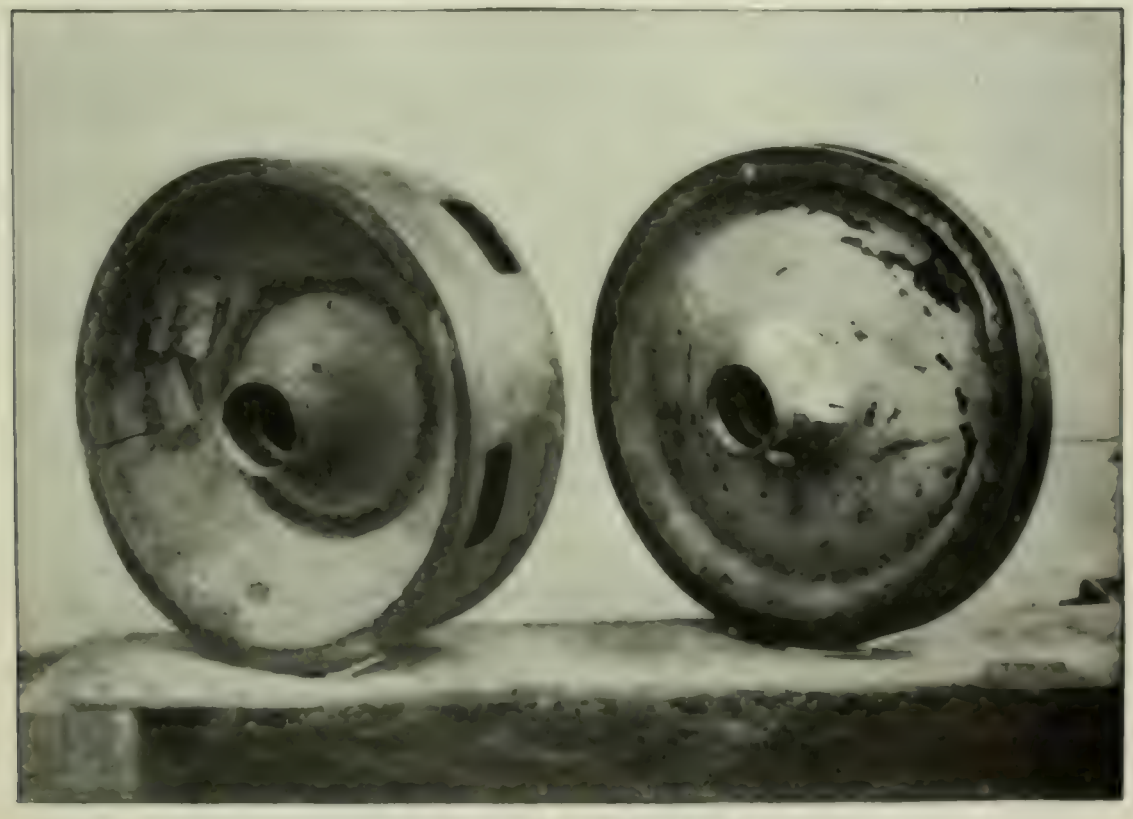

FIG. —*Wheels Nos. 3 and 2*

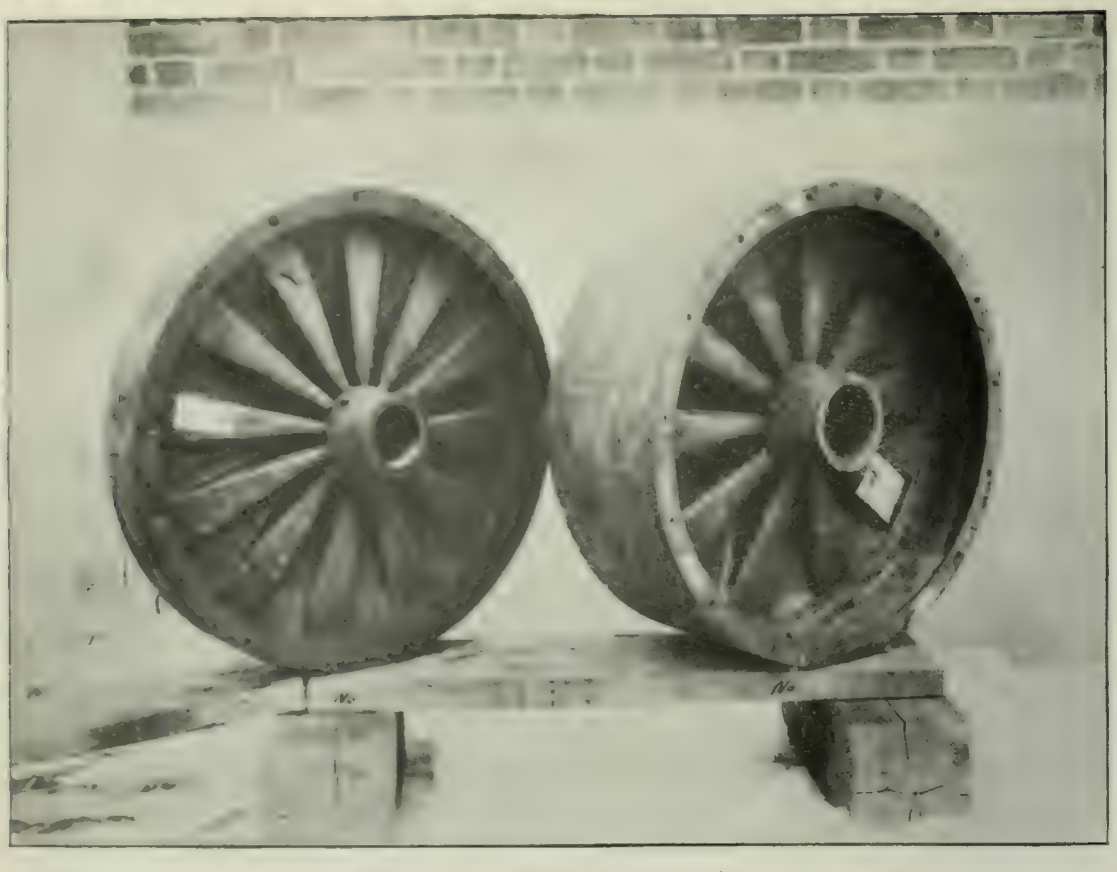

FIG. 31.—*Wheels No. 4 and 5*

FIG. 32.—*Wheel No. 6*

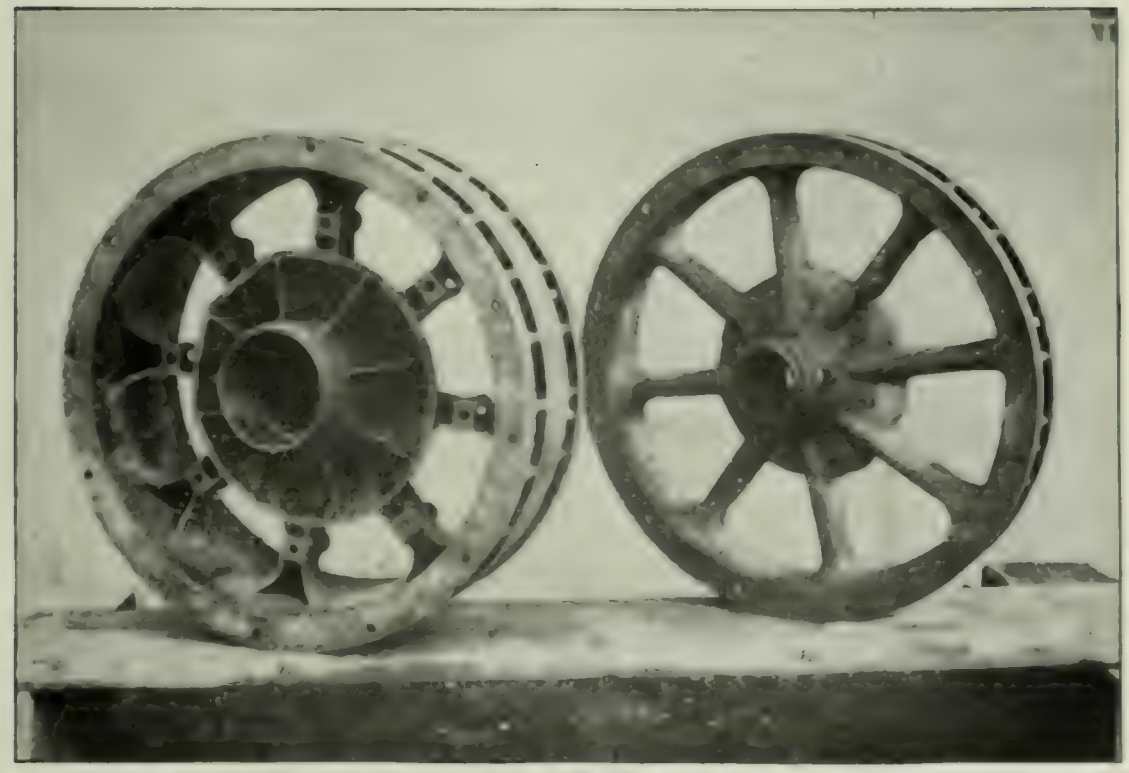

FIG. 33.—*Wheels No. 8 and 7*

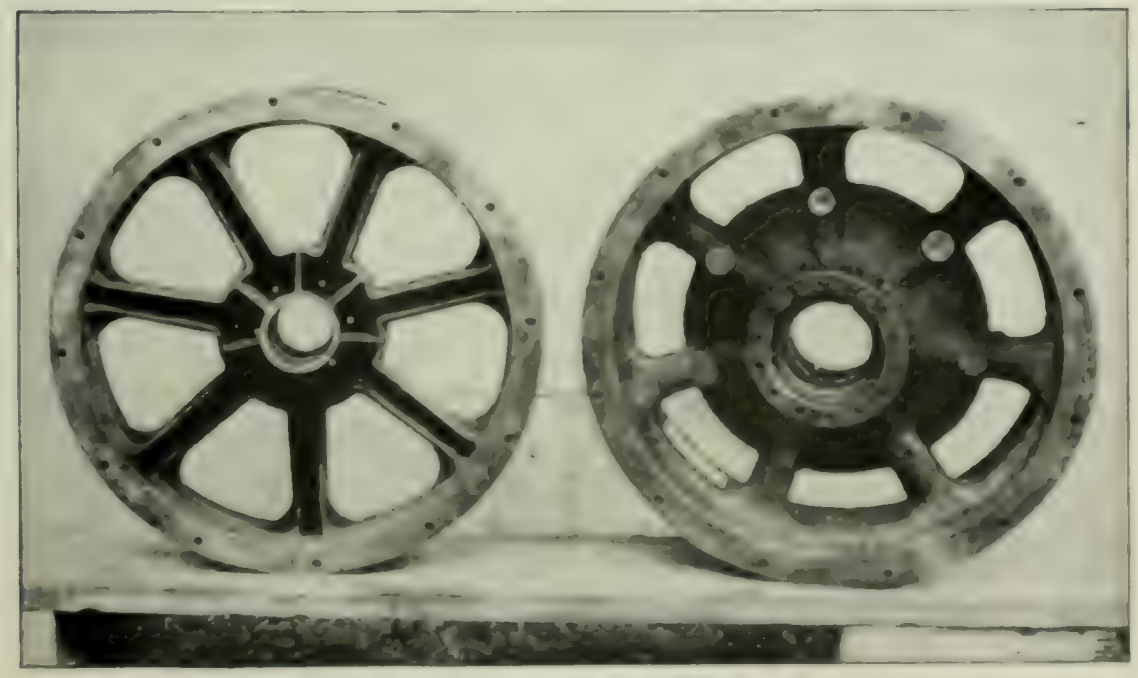

FIG. 34.—*Wheels No. 9 and 10*

FIG. 35.—*Wheel No. 11*

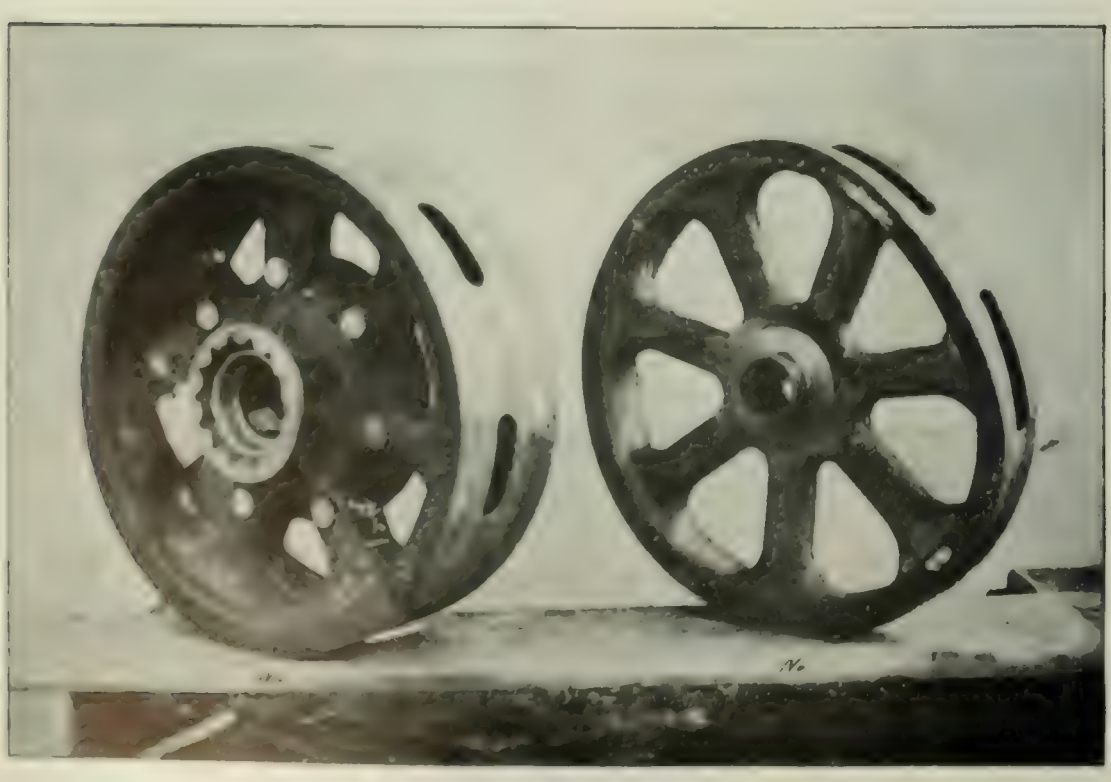

FIG. 36.—*Wheels No. 13 and 12*

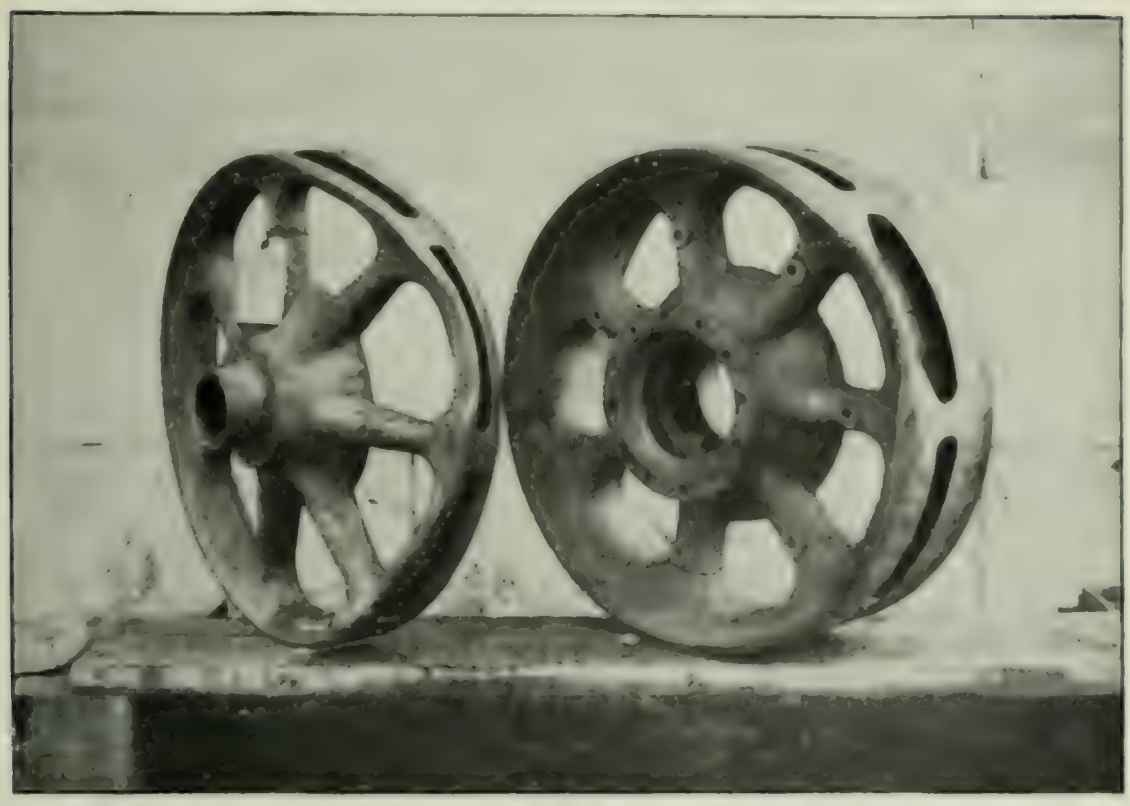

FIG. 37.—*Wheels No. 14 and 15*

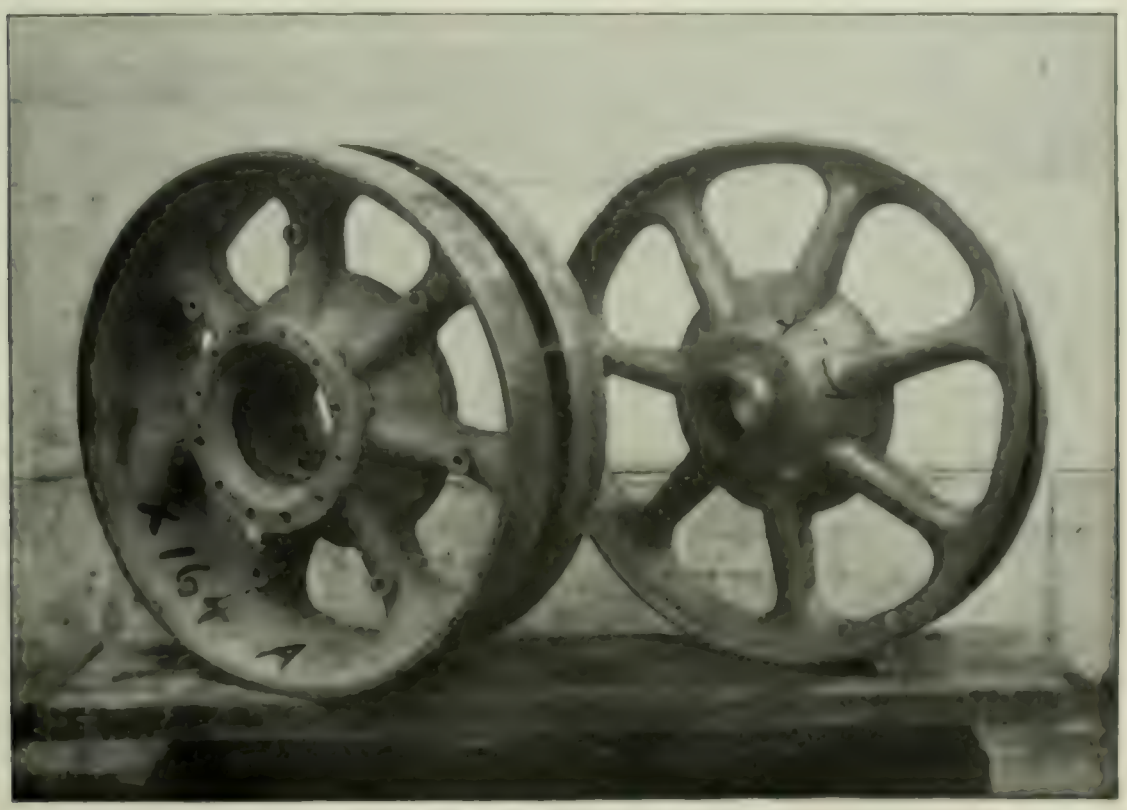


FIG. 38.—*Wheels No. 17 and 18*

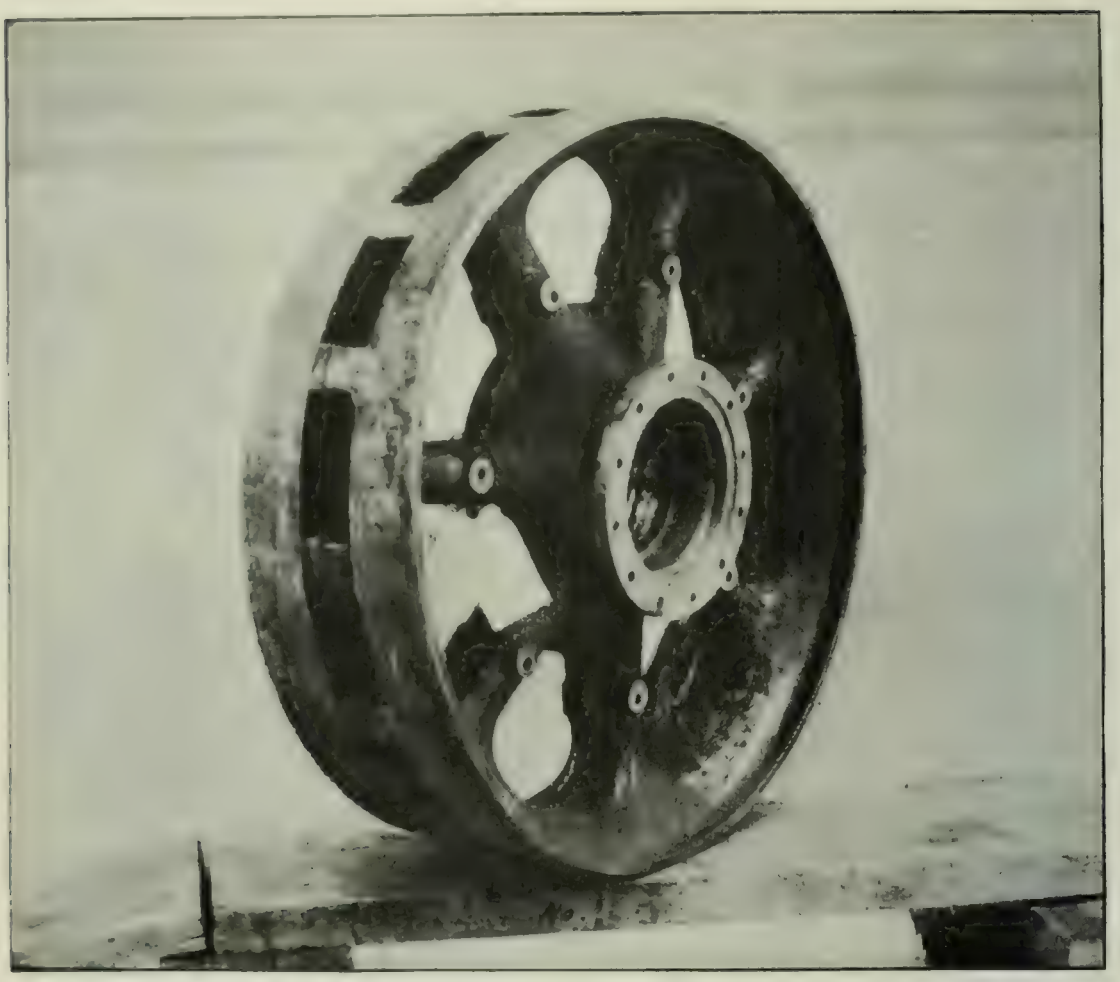

FIG. 39.—*Wheel No. 18*

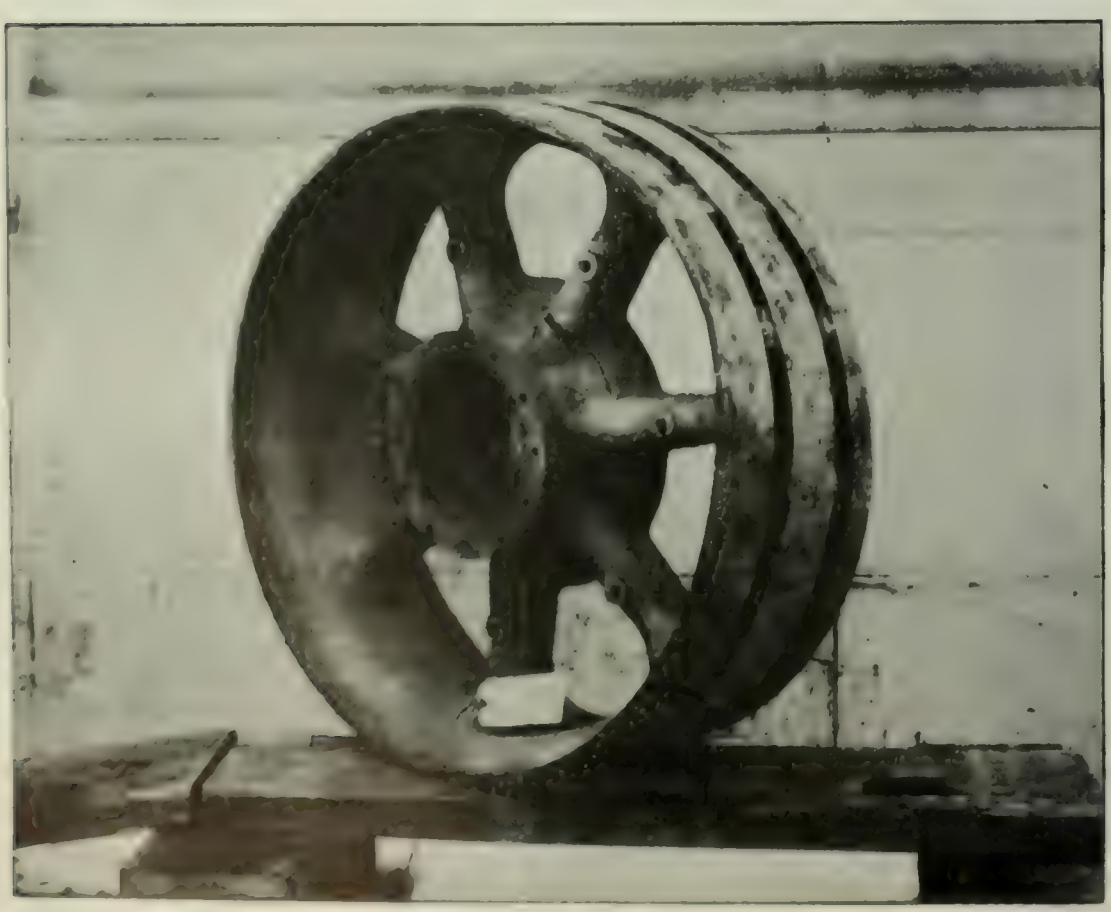

FIG. 40.—*Wheel No. 19*

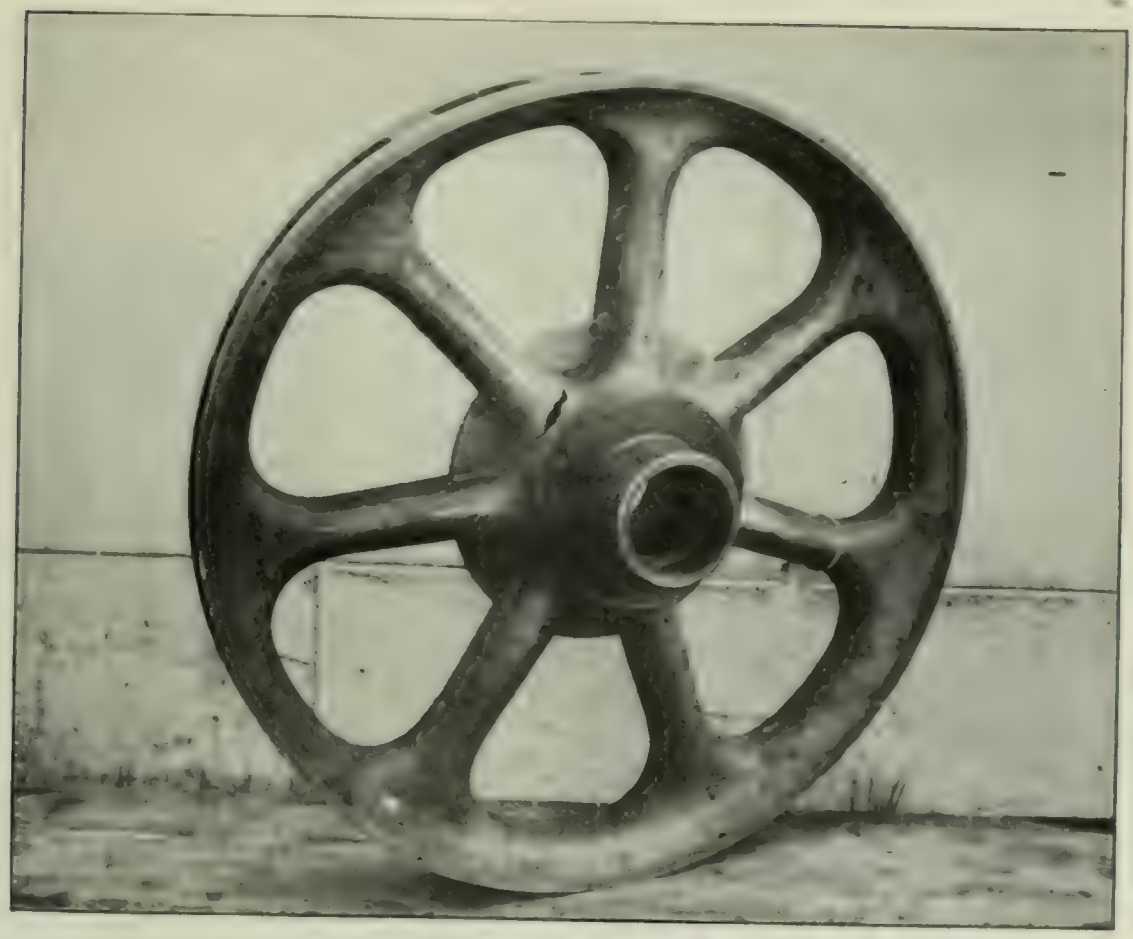

FIG. 41.—*Wheel No. 29*

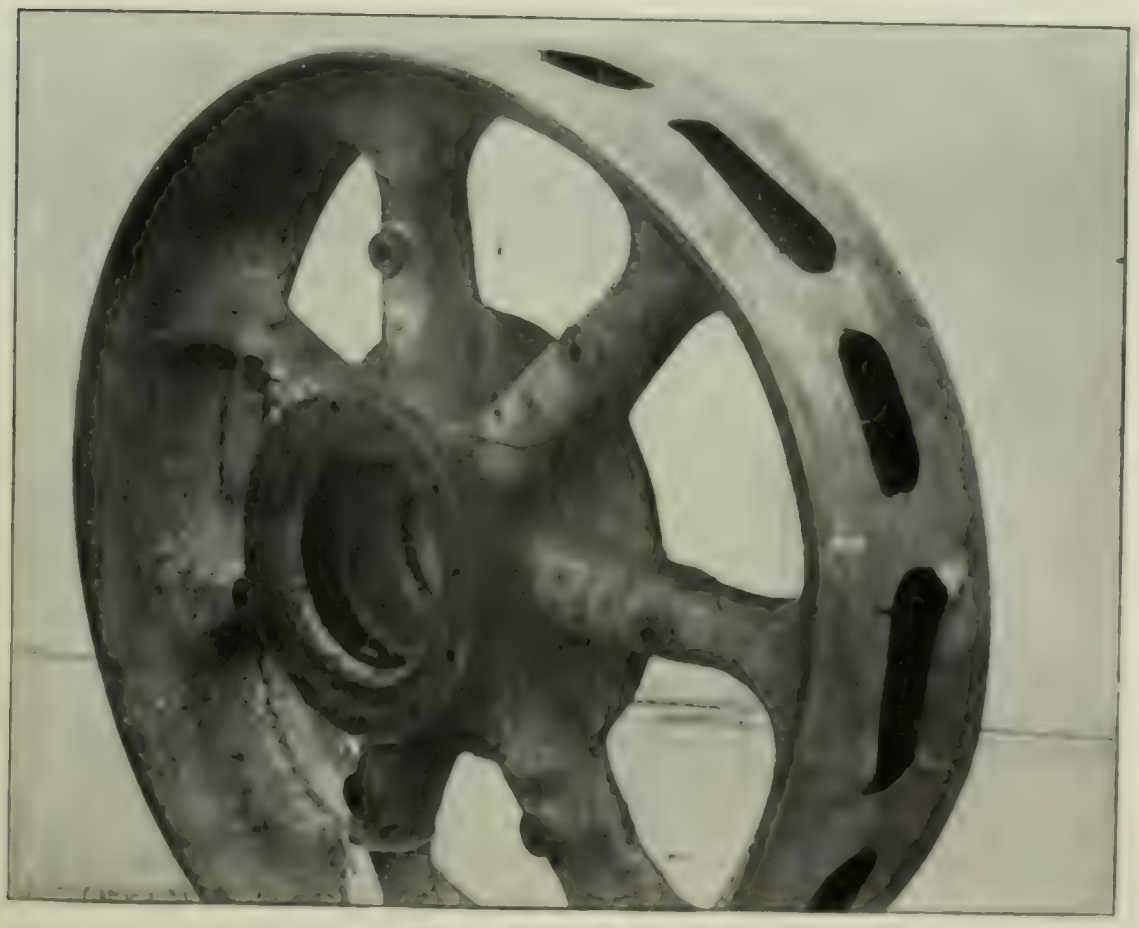

FIG. 42.—*Wheel No. 31*

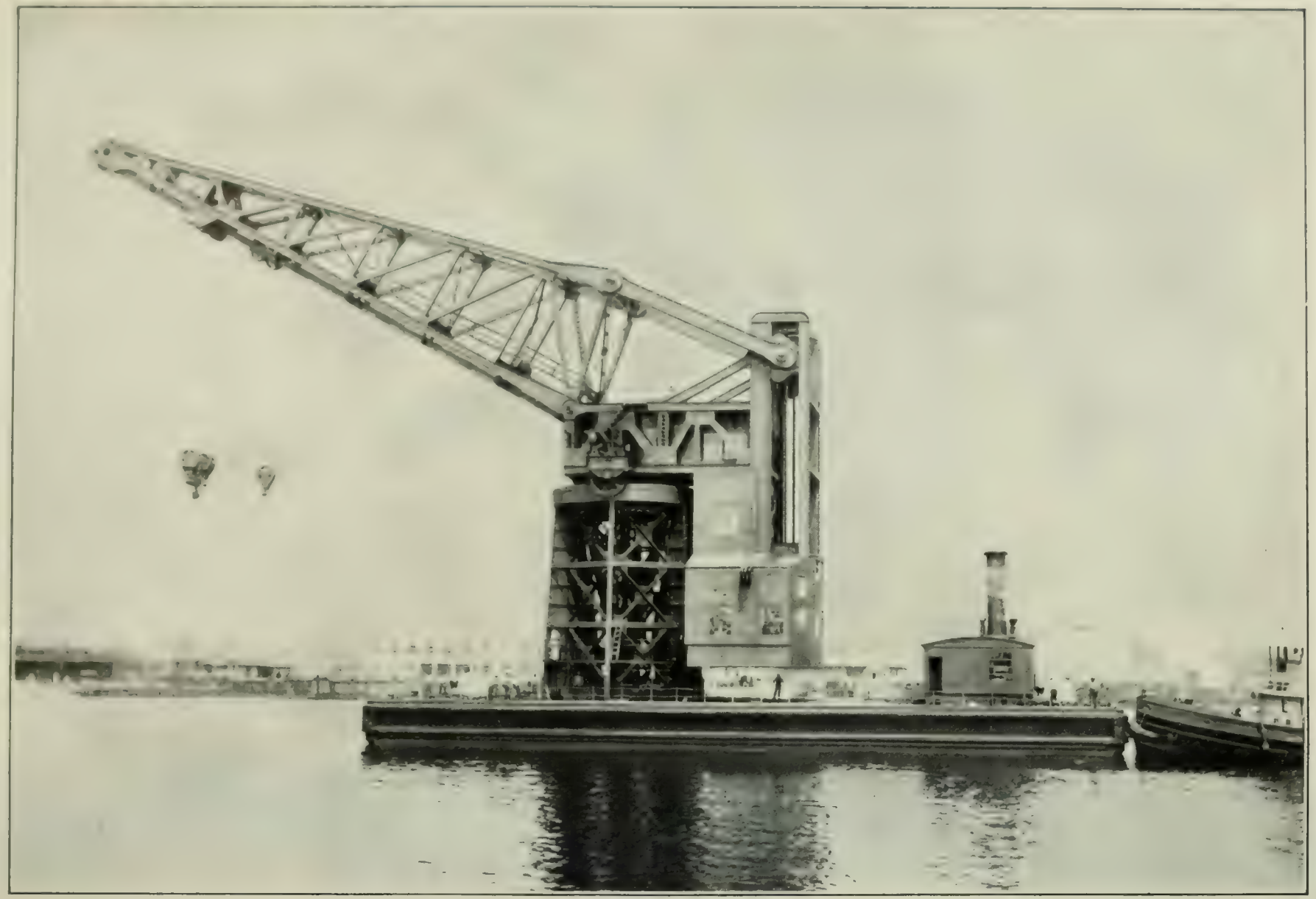

FIG. 1.—*Crane under no load*

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

## No. 151

# LOAD STRAIN-GAGE TEST OF 150-TON FLOATING CRANE FOR THE BUREAU OF YARDS AND DOCKS U. S. NAVY DEPARTMENT

BY

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*Bureau of Standards*

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By Louis J. Larson and Richard L. Templin

## CONTENTS


| | Page |
|---|---|
| I. Introduction | 4 |
| 1. Purpose of test | 4 |
| 2. Description of the crane | 4 |
| II. Procedure of test | 5 |
| 1. Preparation for test | 5 |
| (*a*) Members in which stresses were measured | 5 |
| (*b*) Location and numbering of gage lines | 6 |
| (*c*) Superstructure gage lines | 6 |
| (*d*) Pintle gage lines | 6 |
| (*e*) Deck gage lines | 7 |
| (*f*) Tower leg gage lines | 7 |
| 2. Instruments used | 10 |
| (*a*) Berry strain gage | 10 |
| (*b*) Deflection readings | 10 |
| 3. Method of loading | 10 |
| 4. Loading schedule | 10 |
| (*a*) Table of loading | 11 |
| III. Discussion of Results | 12 |
| 1. Test conditions | 12 |
| (*a*) Standard bars | 12 |
| 2. Method of reducing data | 12 |
| (*a*) Assumed no load condition | 13 |
| 3. Method of representing results | 14 |
| (*a*) Strain gage results | 14 |
| (*b*) Deflection results | 14 |
| 4. Test results | 14 |
| (*a*) Deck | 14 |
| (*b*) Tower | 16 |
| Strain gage readings | 16 |
| Average stresses in the tower | 16 |
| Distribution of the stress across the tower leg | 19 |
| Behavior of the tower under load | 20 |
| Magnitude of the stresses in the tower | 21 |
| Deflection readings | 22 |
| (*c*) Pintle | 25 |
| Behavior of the pintle under load | 26 |
| Magnitude of the stresses in the pintle | 27 |
| (*d*) Superstructure | 28 |
| Vertical posts of the superstructure | 29 |
| Jib members | 29 |
| Struts for the luffing-screw guides | 30 |
| Side diagonals of the superstructure | 30 |
| Front diagonals of the superstructure | 31 |
| (*e*) Screws | 31 |
| IV. Summary and suggestions | 33 |
| 1. Summary | 33 |
| 2. Suggestions | 33 |

## I. INTRODUCTION

### 1. PURPOSE OF TEST

At the request of the Bureau of Yards and Docks of the Navy Department, arrangements were made to take strain-gage measurements on some of the important members of a 150-ton (336 000-pound) revolving, floating crane built for use in the navy yard at Norfolk, Va. The test was of special interest and importance to the Navy Department for two reasons: (1) The structure as a whole is statically indeterminate; and a wide difference of opinion as to the distribution of stress among the various members of the crane while under load was found to exist among engineers who had been engaged in designing and checking the structure. (2) The importance of having a more complete knowledge of the loads carried by the various members was forcibly emphasized by the failure of a similar structure built for use on the Panama Canal.[1]

Furthermore, the size of the structure and the unknown behavior of some of its members made a strain-gage test very desirable.

All of the strain-gage measurements were made by the authors.

The Norfolk Navy Yard furnished men for recording the data taken, the material and labor for proof loading the structure, and the photographs reproduced in this report.

The engineers who operated the crane mechanism during the test were furnished by the Wellman-Seaver-Morgan Co., the builders of the crane.

The Bureau of Yards and Docks cooperated in selecting the members on which the strain-gage measurements were taken and furnished the necessary data and drawings.

### 2. DESCRIPTION OF THE CRANE

The crane, as a whole, represents the most advanced type of revolving floating cranes of large capacity.

The jib of the crane is essentially a tapering Pratt truss hinged to the superstructure at the lower chord and connected to the luffing screws at the upper chord by suitable links. The length of the links and the location of the luffing screws are such that a nearly direct pull is exerted on the upper chord of the jib for all positions.

The superstructure, exclusive of the jib, consists of two subdivided triangular trusses rigidly connected by cross bracing. In

[1] Eng. News, p. 913, May 13, 1915.

addition to supporting the jib arm the trusses carry the machinery house and jib-arm counterweight on the ends opposite the jib arm. The entire revolving load is transmitted by the triangular trusses to the pontoon through a pintle.

The pintle is an inverted pyramidal-shaped member, built up of four posts, which transmits its load at the apex to a thrust bearing on the deck of the pontoon.

A tower, consisting of six legs, arranged in the form of a hexagon, supports this pintle laterally. The legs of this tower are carried through the deck to the framing of the pontoon. The system of bracing between the legs is intended to make the whole structure of the tower act as a unit. The entire tower will then deform under load as a cantilever beam instead of allowing the individual columns to carry the lateral forces independently. Further, the tower is framed into the hull in such a manner as to make the pontoon act as a large girder in resisting the forces induced by a crane load.

The lateral thrust at the top of the tower is transmitted to the pintle through rollers running on circular tracks framed between the tower columns and pintle posts. The pintle, rotating within the tower, makes it possible to revolve the superstructure with the live load to any position.

Throughout the full horizontal movement of the crane the jib may be raised through an angle of approximately 52° from its lowest position, at which position the lower chord of the jib makes an angle of approximately 27° with the horizontal.

## II. PROCEDURE OF TEST

### 1. PREPARATION FOR TEST

The members about which it was desired to secure information concerning the amount of stress developed in transmitting the crane load to the pontoon, were chosen after a study of the drawings and a discussion with the Bureau of Yards and Docks, Navy Department.

(*a*) MEMBERS IN WHICH STRESSES WERE MEASURED—It was decided to take readings—

1. At various points on the deck, to determine the magnitude and if possible the position of maximum stress in the upper deck plate.

2. On the tower members, to determine whether the tower acted as a unit.

3. Around the manhole in the tower legs, to find the effect of such an opening.

4. On the pintle, to determine the magnitude of the stress in these members.

5. On various members of the superstructure, to determine the manner in which the loads were carried down to the pintle.

Considerable difference of opinion existed among designers as to which members would carry the applied loads. The jib member (gage lines *C 1*, *C 2*, *C 3*, and *C 4*) attracted particular interest because of the failure of the corresponding member in the crane built for the Panama Canal.

(*b*) Location and Numbering of Gage Lines.—Gage lines were always placed on two opposite sides of every member tested and, where possible, on all four sides to detect any bending. The location of the gage lines is shown in Fig. 15.

(*c*) Superstructure Gage Lines.—In general, for the superstructure, where two gage lines are shown on the same side of a member, the odd numbers are on the outer and the even numbers are on the inner side.

Gage lines *C 1*, *C 2*, *C 3*, and *C 4* are located 6 inches above the gusset plate at the lower end of the member.

Gage lines *R 1*, *R 2*, *R 3*, and *R 4* were located on the edge of the cover plate and about 2 inches from the end of the upper gusset plate. *R 13* and *R 14* were near the middle of the strut. *R 5*, *R 6*, *R 7*, and *R 8* were located about 7 inches below the upper splice plate. Gage lines *R 9*, *R 10*, *R 11*, and *R 12* were on the right (when facing jib) diagonal of front cross truss. They were located about 20 inches from the lower gusset plate. *R 15*, *R 16*, *R 17*, and *R 18* were similarly located on the right (facing jib), diagonal of the truss framing into the rear pintle post. In this one case *R 15* and *R 16* are below the member, and *R 17* and *R 18* are above, the odd numbers in each case being on the inside.

(*d*) Pintle Gage Lines.—In numbering the gage lines on the pintle, the following scheme was followed throughout. Standing within the pintle and facing the jib the pintle post in front was called post No. 1. Proceeding in a clockwise direction gage line *P 1* is on the left side of post No. 1 and gage line *P 2* is on the right side. The remaining posts are numbered *2*, *3*, and *4*. Similarly, the gage lines on the other posts are numbered *3*, *4*, *5*, *6*, *7*, and *8*, respectively, for the lower tier. The second and third tiers are similarly numbered from *P 11* to *P 18*, and from *P 21* to

*P 28*, respectively. The gage lines for each tier were located near the midheight of the panels of the pintle as formed by the diagonal bracing.

(*e*) DECK GAGE LINES.—The gage lines on the deck of the pontoon were laid out for the purpose of checking the computed locations of the maximum bending moments and the stresses. With a load of 150 tons, and jib in center-line position, the maximum bending moment as computed should be 40 feet from center of tower, on the center line of the pontoon, between the tower and the engine house. At this location a gage line *D 2*, was placed and 2 feet each side of it, on the same center line, gage lines *D 1* and *D 3* were placed. Other gage lines, *D 4*, *D 5*, *D 6*, *D 7*, *D*, *8* and *D 9* were placed over the longitudinal bulkheads and girders of the pontoon to the right of the center line looking forward, parallel to the gage lines *D 1*, *D 2*, and *D 3* and in the same relative positions. For checking the bending moment and deck stresses with jib abeam, the gage lines *D 21*, *D 22*, *D 23*, *D 24*, *D 25*, *D 26*, *D 27*, and *D 28*, were placed over the center cross bulkhead adjacent and at right angles to the longitudinal deck gage lines previously mentioned. (See Fig. 2.) Four gage lines, *D 31*, *D 32*, *D 33*, and *D 34*, were located at the forward corners of the engine house to determine whether there were excessive stresses in the deck due to discontinuity of the deck plates. These gage lines were placed in pairs at right angles to each other in order to determine the stress in both directions.

(*f*) TOWER LEG GAGE LINES.—Strain-gage readings were taken upon two opposite tower legs. The forward tower leg was to the right and the aft tower leg to the left of the center line of pontoon. Readings were taken at two levels on each tower leg. The lower set of readings was taken between the first and second levels of horizontal lateral bracing, where the manholes or passageways are cut in the tower legs, and the upper set was taken just above the second level of horizontal lateral bracing. The gage lines were arranged in pairs so that all the odd numbers are on one side of the tower legs and the even numbers on the other—that is, *T 2* is opposite *T 1*, *T 4* opposite *T 3*, etc. Readings were taken on the outer flanges, on the web adjacent to the manhole, and on the inner flanges of the tower leg at the lower level, and on the outer and inner flanges of the tower leg at the upper level. (See Fig. 3.)

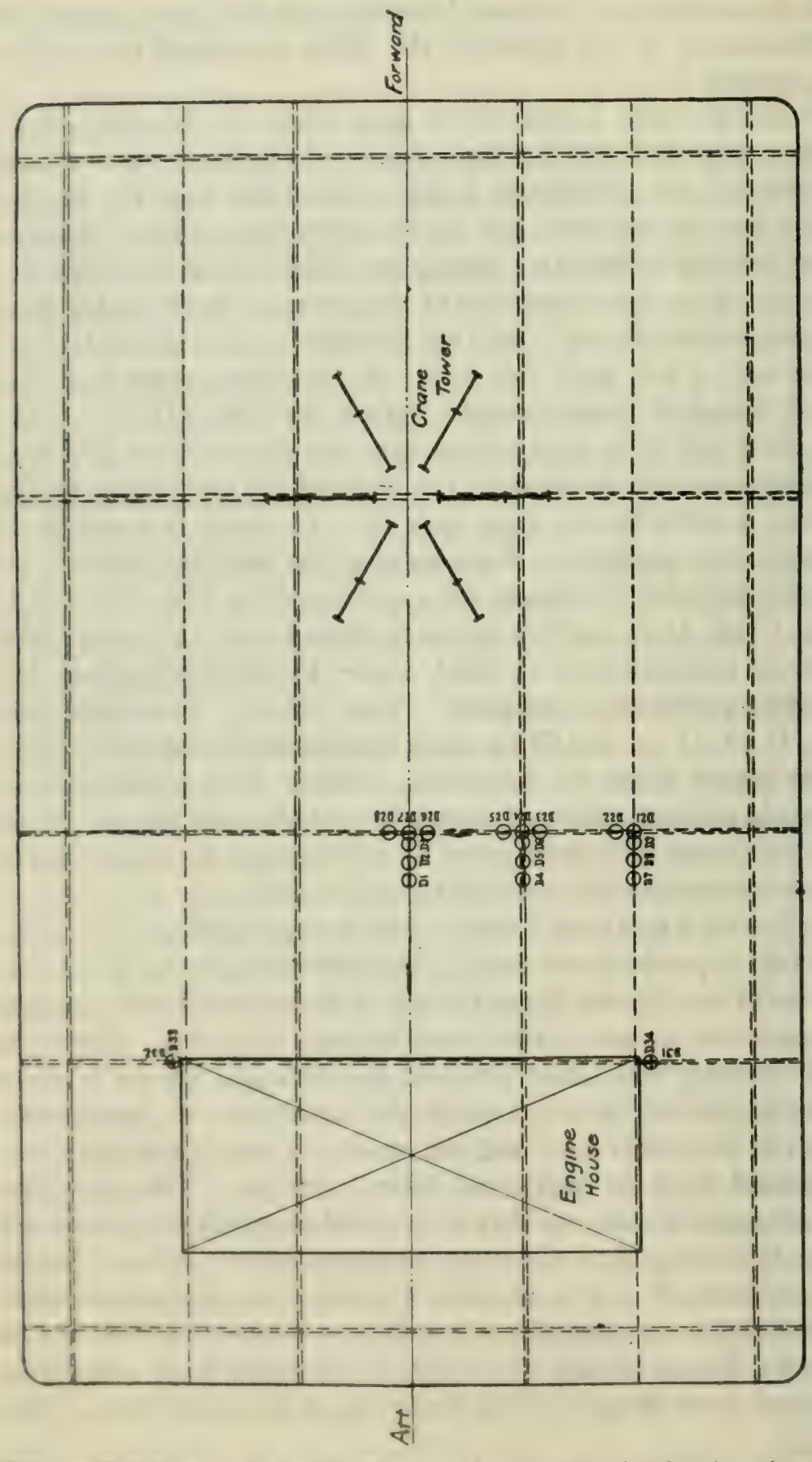
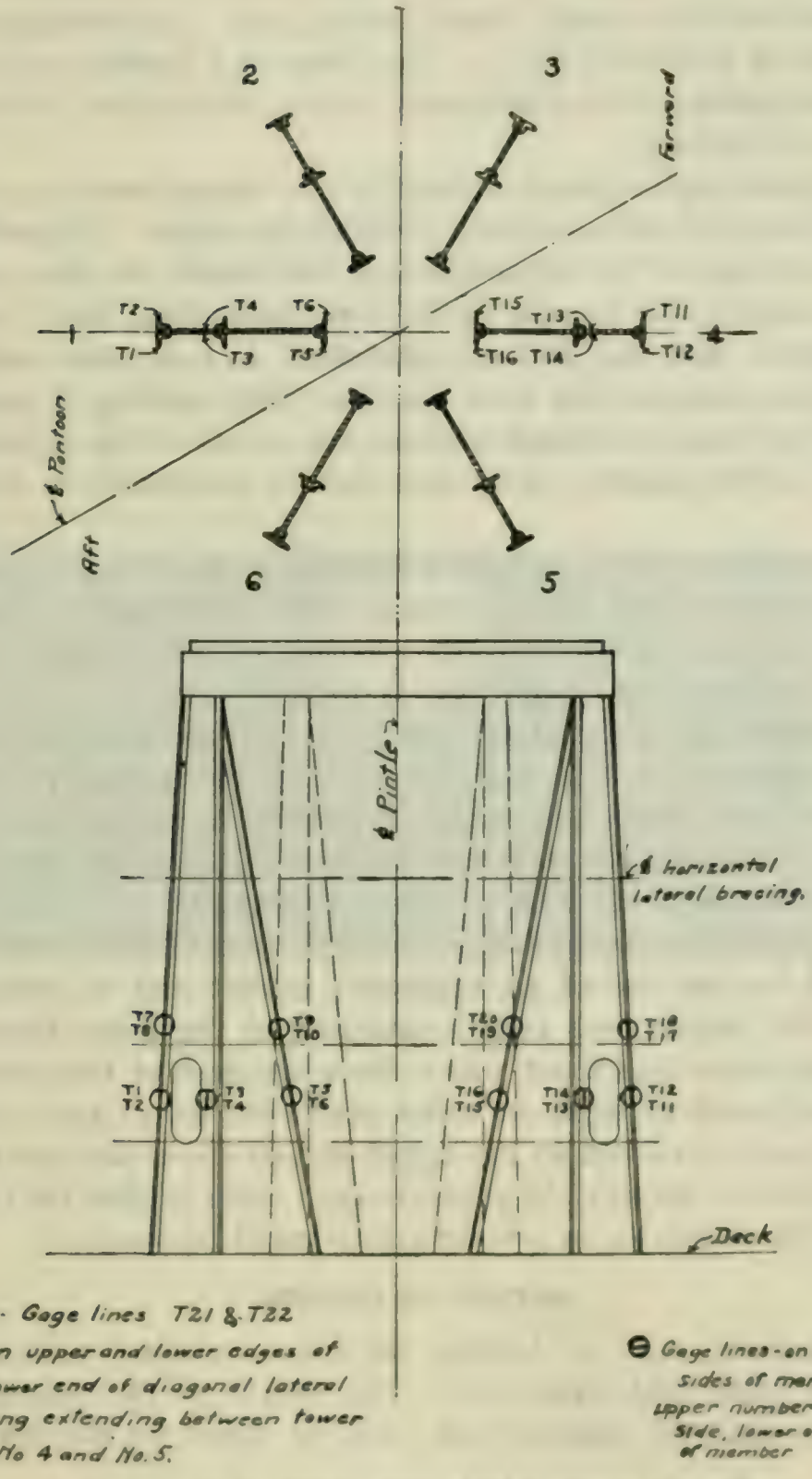



FIG. 2.—*Deck plan of 150-ton floating crane pontoon, showing location of strain-gage readings*




Note:- Gage lines T21 & T22 are on upper and lower edges of the lower end of diagonal lateral bracing extending between tower posts No 4 and No. 5.

⊖ Gage lines - on opposite sides of member upper number on near side, lower on far side of member

FIG. 3.—*Sketch of tower of crane, showing location of gage lines*

### 2. INSTRUMENTS USED

(*a*) BERRY STRAIN GAGE.—The strain-gage measurements were all taken with a 10-inch Berry strain gage. An instrument of this type is shown in Fig. 4. For those not familiar with it a brief description of the instrument and of the method of using it may be of interest.

The strain gage consists essentially of a frame carrying a fixed point at one end and a movable point at the other. The movable point is the end of the short arm of a bell crank, the long arm of which actuates the plunger of an Ames indicating dial. In the instruments used, the dial was graduated to 0.001 inch and the multiplying ratio of the lever was five, thus making it possible to read the change of length between the points of the instrument directly to the nearest 0.0002 inch and by estimation to 0.00002 inch.

The gage lines were established by drilling small holes 10 inches between centers with a No. 56 twist drill. The holes, forming a gage line, must be on the same element of the member if the longitudinal stress in the member is desired.

In making an observation, the points of the instrument are inserted in the gage holes and the resulting dial reading recorded.

It is evident that the changes in length for various load conditions as indicated by such dial readings will give the data from which the stress in the member may be computed.

(*b*) DEFLECTION READINGS.—The deflection of the tower was obtained by the use of an engineer's transit and a graduated scale. The transit was rigidly attached to the outer flange of one of the tower legs about 5 feet above the deck of the pontoon. It was adjusted to sight on scales graduated to 0.1 inch, which were securely attached to the upper end of the same tower leg. The scales were set at right angles to each other so that the movement of the tower leg in two directions could be observed.

### 3. METHOD OF LOADING

The material used for loading the crane consisted principally of armor plate and scrap iron. The weight of the pieces was known so that the desired load could be lifted by the hoisting hook.

### 4. LOADING SCHEDULE

The schedule of loading was so chosen that each member on which measurements were to be taken was subjected to the maximum possible range of stress.

FIG. 4.—*Berry strain gage*

It is evident from an inspection of the crane that the minimum stress or maximum reversed stress occurs with the jib in its highest position with no live load being lifted. In this position the positive moment due to the dead weight of the jib is greatly reduced. For this reason the initial strain-gage measurements were taken with the jib up. Observations were then made with the jib down under the three conditions of no load, 150-ton (long) hook load, and 180-ton hook load.

It was also desired to find the effect of changing the jib location from the center line (over the end of the pontoon) to a position abeam (over the side of the pontoon). Readings were therefore taken on the members affected by this change with the jib located in both positions.

To get the maximum stress in a leg of the tower, a set of observations was made on these members when the jib was located directly over them. No readings were taken on members in which no change of stress was expected.

(*a*) TABLE OF LOADING.—The following table gives concisely the conditions of loading and the gage lines on which observations were made:

**TABLE 1.—Conditions of Loading and the Gage Lines on Which Observations Were Made**

| Load in tons | Position on jib | Reading on members |
|---|---|---|
| 0 | Jib up on center line | All members. |
| 0 | Jib down on center line | Do. |
| 0 | Jib up abeam | Tower and deck. |
| 150 | Jib down on center line | All members. |
| 150 | Jib down abeam | Tower and deck. |
| 180 | Jib down on center line | All members. |
| 180 | Jib down abeam | Tower and deck. |
| 180 | Jib down over post | Tower. |

For their own information and as a check on their calculations, the Navy Department measured the angle of list in various directions under the several conditions of loading. In this report we are concerned only with the strain-gage and the deflection measurements.

In the position designated as "jib down" this member was in its lowest possible position only under the no-load condition. Under the load the jib was luffed until the reach beyond the edge of the pontoon was the maximum required by the specifications.

## III. DISCUSSION OF RESULTS

### 1. TEST CONDITIONS

It is readily seen that in the determination of results which depend upon a measurement of the deformation of the material under stress, the temperature and other weather conditions become important factors. A large change of temperature may cause as great a change of length of the member as the application of a load. During this test the weather conditions varied from very hot and clear to cool and rainy.

(*a*) STANDARD BARS.—It is customary to take readings on unstressed bars of the same material as the structure known as "standard bars." From these readings it is presumed that it is possible to correct the test observations for changes due to temperature. The use of these bars also eliminates possible errors due to accidental change in the adjustment of the instrument.

Standard bars serve very well for temperature correction provided their changes correspond to the temperature changes of the members. However, during this test some of the members were in the bright sun and others in the shade when one set of observations was taken; at another time of day, or with the jib in a different position, the conditions might be reversed, thus making it impossible to place the standard bars so that their temperature would be representative of that of all the members.

Conditions were further complicated by a rain which caused many of the gage holes to rust, thus probably changing the readings to some extent.

### 2. METHOD OF REDUCING DATA

A preliminary analysis of the data showed that corrections based upon the standard bar readings gave quite satisfactory results for for practically all cases. However, in the case of the 150-ton load, the indicated stresses in the pintle and superstructure appeared to be about 2000 pound per square inch too low in compression and an equal amount too high in tension when compared with those obtained for the zero and 180-ton load. Since the magnitude and sign of the correction which appeared to be required was practically the same for all members whether subjected to a large or small stress, to tension or compression, it seems logical to apply such a correction especially in view of the conditions under which the test was conducted. This correction has therefore been made throughout the computations for this report.

In the case of the deflection readings on the tower an adjustment was found necessary. The observations taken as the loading proceeded have been discarded, as it was found that the instrument was generally disturbed between consecutive observations. The deflection observations, taken as the jib was continuously rotated with the 180-ton load, have been used in this report. Although the actual zero for this set could not be obtained directly, the readings are considered reliable, since the instrument was not disturbed. The zero deflection, in each direction, was assumed as midway between the extremes and the deflection readings adjusted accordingly.

(*a*) Assumed No Load Condition.—It will be recalled (see loading schedule) that the initial strain-gage readings were taken

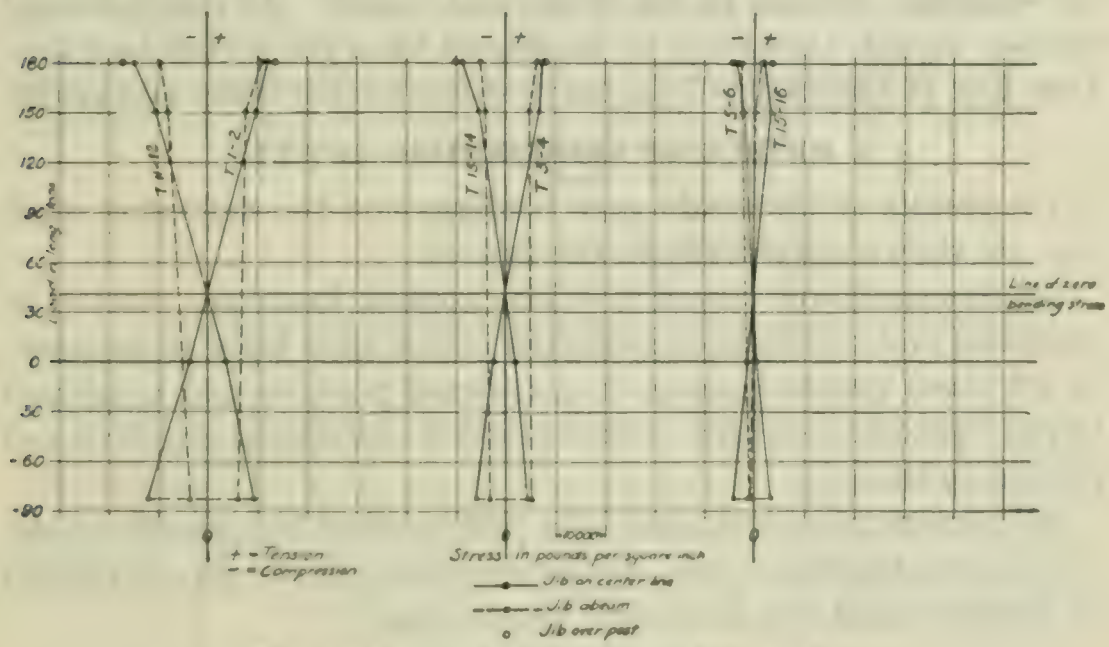



Fig. 5.—*Average load-stress curves for tower legs*

with the jib in its highest position with no load on the hook and in making the stress calculations this condition has been assumed to give zero stress. For convenience in plotting the load-stress curves the condition of the jib in its lowest position with no hook load was considered the condition of no load on the structure. It was therefore necessary to calculate a hook load that would produce stresses in the structure equivalent to that caused by lowering the jib. This calculation was based on the data (see Fig. 5) obtained from the blue prints of the crane as submitted by the Bureau of Yards and Docks.

For the members of the pintle and superstructure, the horizontal reactions at the base of the pintle were used, and it was found that the change in stress in the structure of raising the jib

from the lowest to the highest position was equivalent to applying a negative load (lift) of 68 tons through the center line of the hook with the jib at its lowest position. Similar calculations showed that an upward reaction of 83 tons at the main hook would be required to offset the stresses produced in the tower and deck by lowering the jib. These calculations should be considered as approximate, since the effect of the direct stress due to the application of the live load as well as the effect due to the small change in the list angle which such a hook load would produce have been neglected. From the values of the dead and live load moments, as furnished by the Bureau of Yards and Docks, it has been calculated that a live load of 40 tons, applied to the jib in its lowest position, is just sufficient to balance the dead loads, thus producing zero-bending stresses in the tower and pintle. All the indicated stresses should, therefore, be measured from the 40-ton load line. This line is shown on all the curve sheets for the tower and pintle.

### 3. METHOD OF REPRESENTING RESULTS

The results of the strain-gage readings and the deflection readings are shown graphically in the figures.

(*a*) STRAIN-GAGE RESULTS.—The applied loads are plotted as ordinates and the stresses indicated at the gage lines as abscissæ. In all these graphs tension is considered positive and is plotted to the right of the origin; compression is considered negative and plotted to the left.

(*b*) DEFLECTION RESULTS.—In representing the results of deflection measurements, the angles of rotation of the jib are plotted as ordinates and the deflections as abscissæ.

### 4. TEST RESULTS

(*a*) DECK.—The results of the deck readings will be found on Figs. 6 and 7. The full-line curves represent the stresses obtained with the jib on center line and the dotted-line curves show the corresponding values for the jib abeam. As a reliable indication of the actual stresses developed in the deck, these curves are not satisfactory. It will be seen that a load of 180 tons does not produce a stress proportional to that resulting from the 150-ton load. In many cases the indicated stress is less for the larger load, a condition which is obviously incorrect. The irregularities in the curves are undoubtedly due to the large temperature changes to which the deck was subjected. When exposed to the sun, the deck plate which was covered with asphaltum paint became very hot.

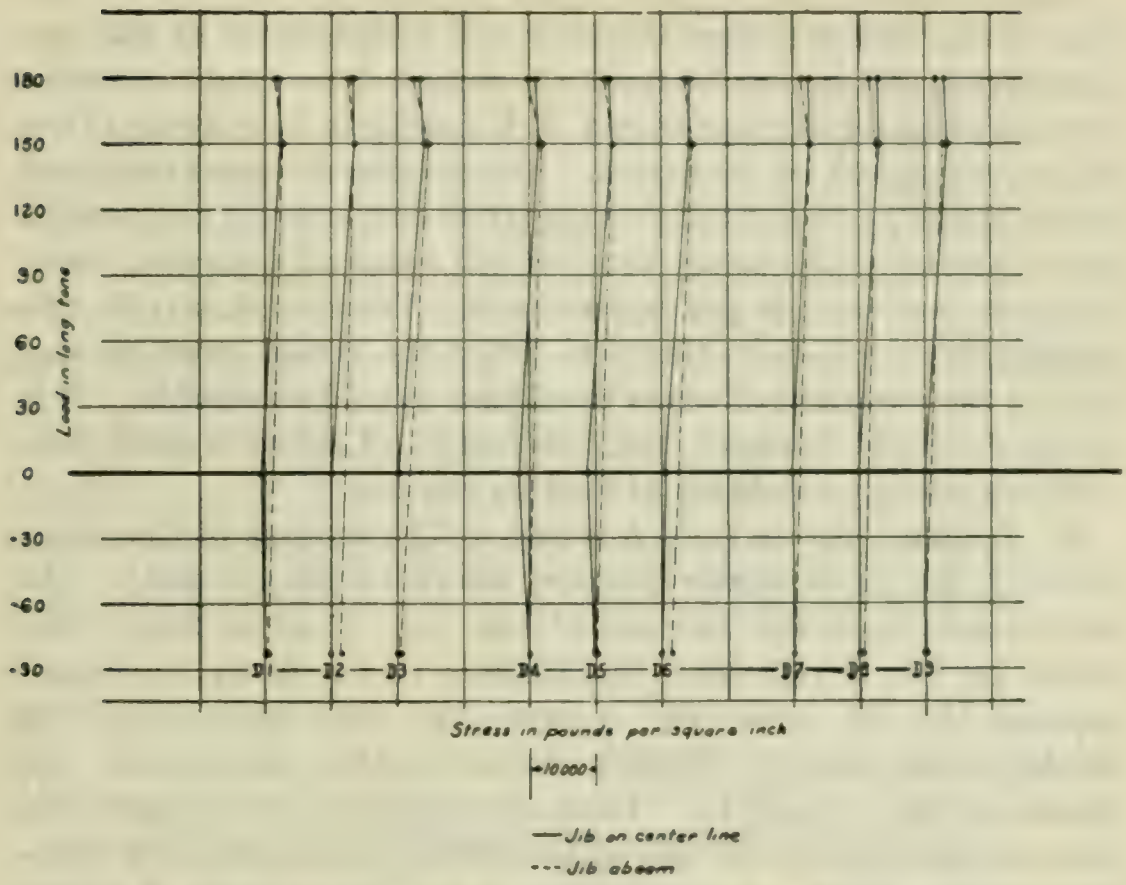



FIG. 6.—*Load-stress curves for deck of pontoon, gage lines D1–D9*

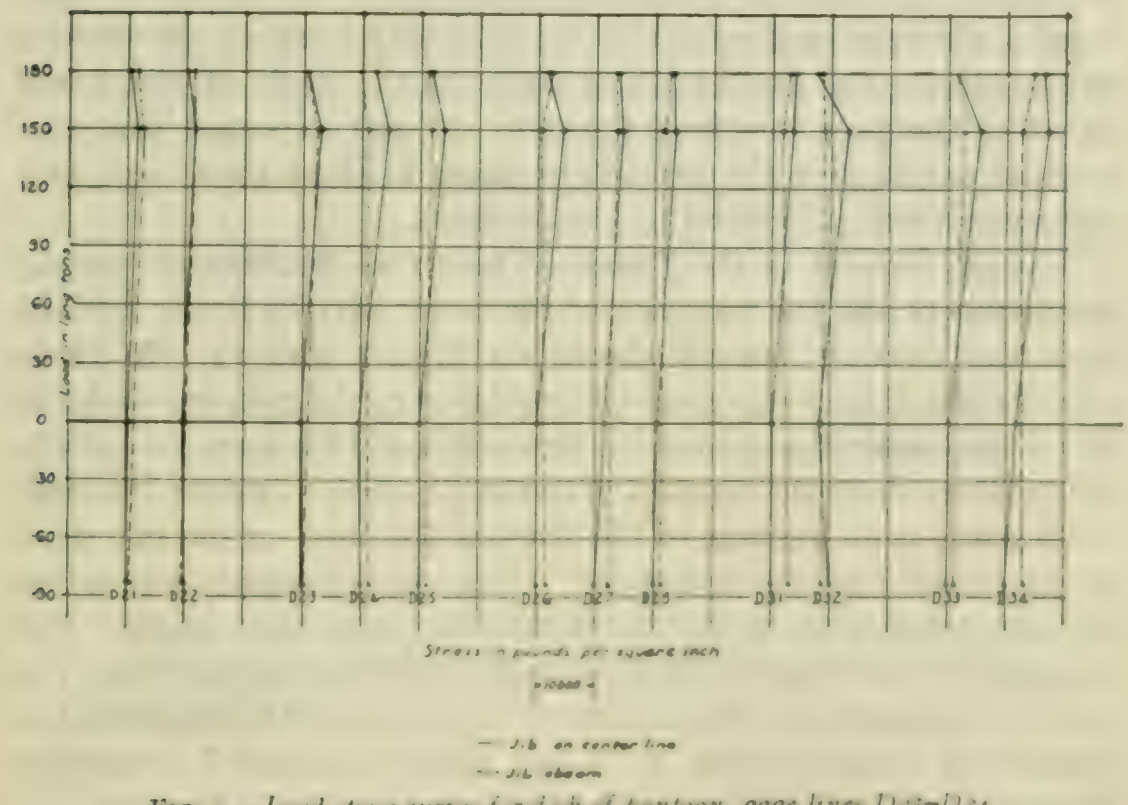



FIG. 7.—*Load-stress curves for deck of pontoon, gage lines D21–D34*

When in the shade of part of the structure or of a cloud, the deck would assume approximately the temperature of the air. Considering the number of times the temperature conditions were actually changed during the test, it is hardly to be expected that the curves should be consistent. The maximum stress indicated is only about 7,000 and the average stress only about 3,000 pounds per square inch. A change of 1° F will cause an indicated stress of nearly 200 pounds per square inch. The uncertainty in the temperature corrections therefore make the actual stress at any load or the variation of stress from load to load unreliable. It is safe to conclude, however, that the margin of safety is more than sufficient for any condition of load on the jib.

(*b*) TOWER.—*Strain Gage Readings.*—The stresses in the tower legs with the jib on center line are shown on Figs. 8 and 9. As will be seen from the location of the gage lines on Fig. 3, the curves on Fig. 8 represent the stresses in the tower leg nearly opposite the jib, while Fig. 9 shows the load-stress curves for the leg under the jib. Similar curves for the "jib abeam" are shown in Figs. 10 and 11. These curves are shown in pairs; the odd numbers are on one side of the tower leg and the even numbers on the other. A comparison of the two curves of a pair shows a very close agreement of stress between the two sides of the tower leg under all conditions of loading. As noted on Figs. 8 and 9, the extra reading at the 180-ton load represents the stresses due to placing the jib directly in line with the posts of the tower on which the gage lines were located. It was expected that this position would give the maximum stress in these tower legs, and this assumption is verified by the readings.

*Average Stresses in the Tower.*—The stress distribution among the members and the behavior of the tower may be better studied from the average curves shown on Figs. 5 and 12. In these curves the full lines represent the results of readings taken with the jib on the center line or over the forward end of the pontoon and the dotted lines show the stresses with the jib abeam or over the side. Each curve is an average of the stresses obtained on the two sides of the member at the same point. Gage lines similarly located on opposite sides of the tower are plotted from the same origin. For example, the average stress for jib on center line at gage lines *T 1* and *T 2* is shown by the full line to the right of the origin in the first set of curves on Fig. 5. Gage lines *T 11* and *T 12* occupy the same relative position on the opposite side of the tower as *T 1* and *T 2*, and the average stresses obtained from these gage lines

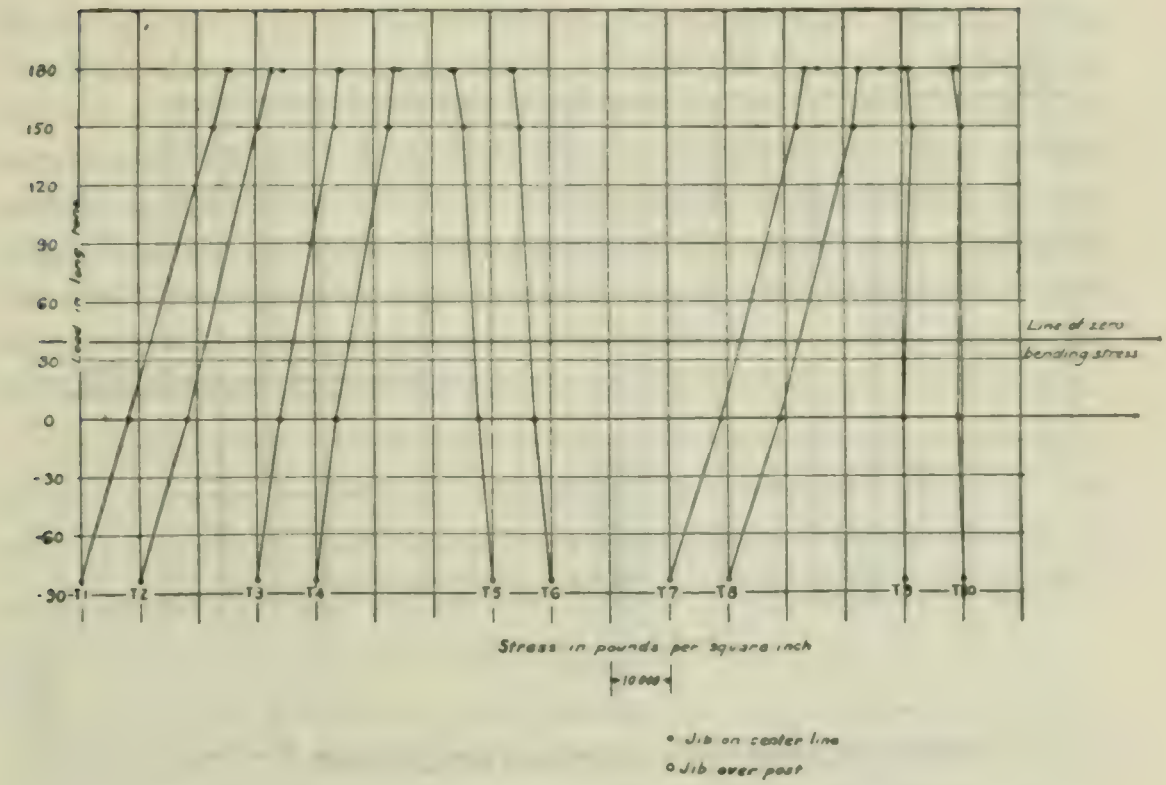



FIG. 8.—*Load-stress curves for tower legs, jib on center line T1–T10*

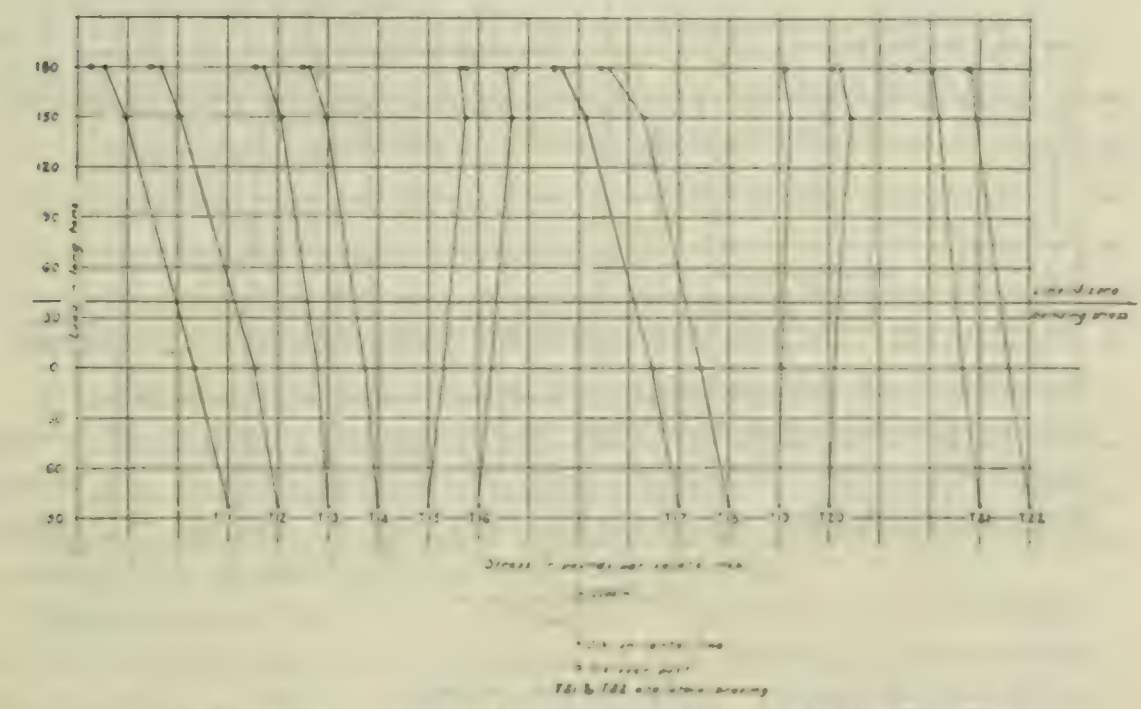



FIG. 9.—*Load-stress curves for tower legs, jib on center line T11–T22*

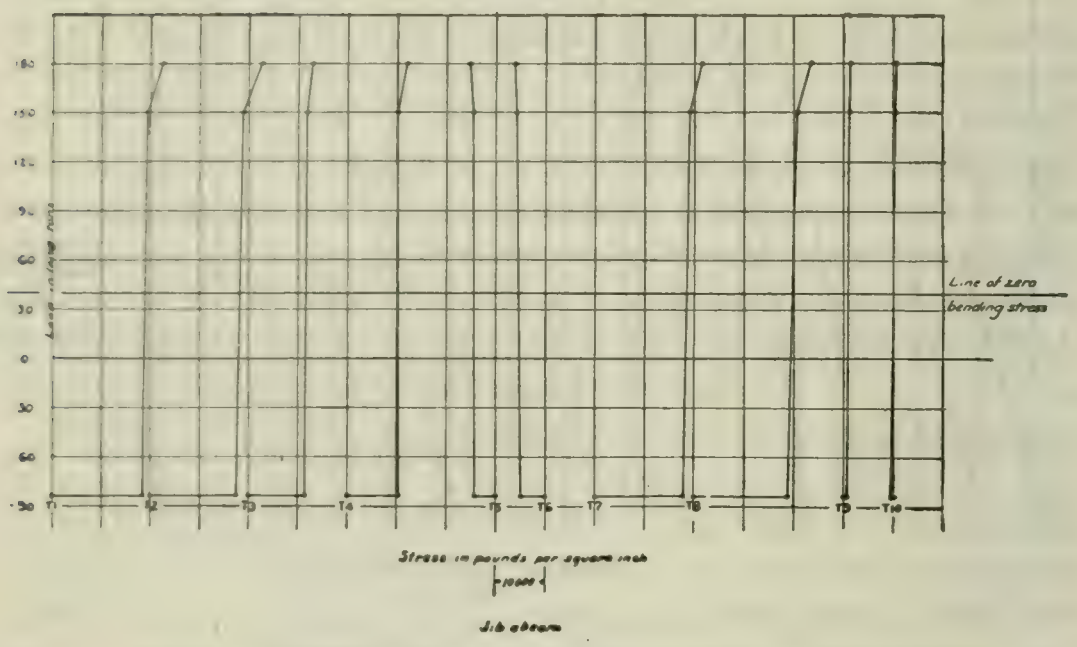



FIG. 10.—*Load-stress curves for tower legs, jib abeam T1–T10*

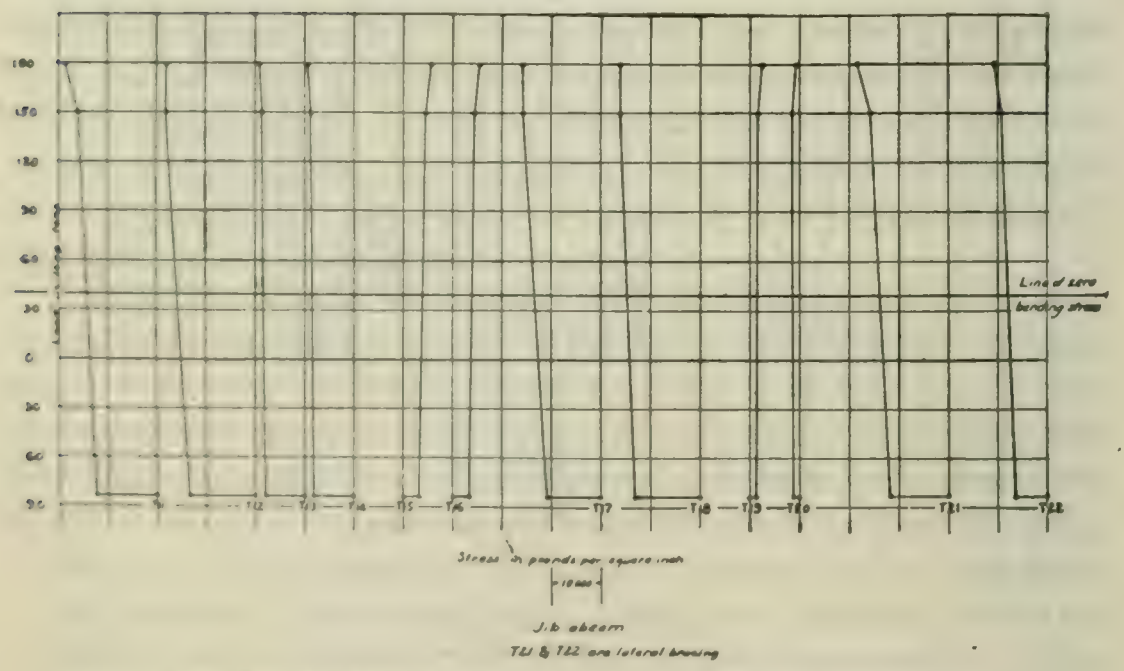



FIG. 11.—*Load-stress curves for tower legs, jib abeam T11–T22*

are therefore represented by the full line to the left of the origin. Similar groups of curves are shown for each location on the tower at which observations were made. From the location of the gage lines it will be seen that the three groups from left to right of curves on Fig. 5 show the conditions of stress at the outer, middle (approximately), and inner edges, respectively, of the tower legs at the level of the center of the manhole. Similarly, the first two groups on Fig. 12 show the stresses at the outer and inner edges of the tower legs at the upper level. (See Fig. 3 for location of tower gage lines.)

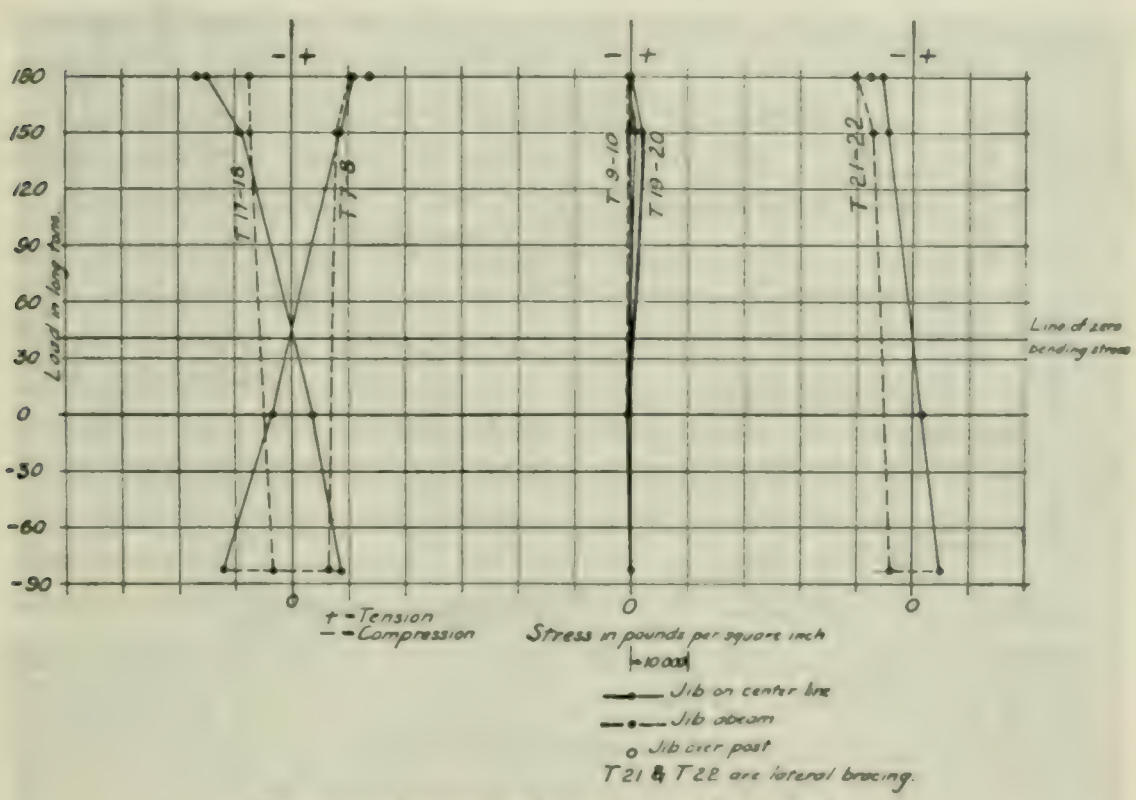



FIG. 12.—*Average load-stress curves for tower legs*

A study of the curves for the jib on center line shows that the stress developed at corresponding points on opposite sides of the tower are equal and opposite within the limits of observational error. It will also be seen that the magnitude of the stress varies considerably across the section of the tower leg.

*Distribution of the Stress Across the Tower Leg.*—To facilitate a study of the variation of stress across the section of the member, the curves on Fig. 13 have been plotted. These curves show the variation in stress at the various points on the tower legs. At the lower level the stresses decrease from a maximum value at the outer edge of the section to zero at a point approximately 2 feet from the inner edge, and then increase with the opposite

sign until the inner edge is reached. At the upper level the point of zero stress, commonly known as the neutral axis, is approximately at the edge of the tower. Although the inner edge of the tower is sloping the neutral plane is almost vertical.

*Behavior of the Tower Under Load.*—This stress distribution throws some light on the method in which the tower acts. If the entire tower acted as a unit the stresses at opposite edges should be equal and opposite, but the neutral axis should be at the center of the tower. If the individual legs acted as canti-

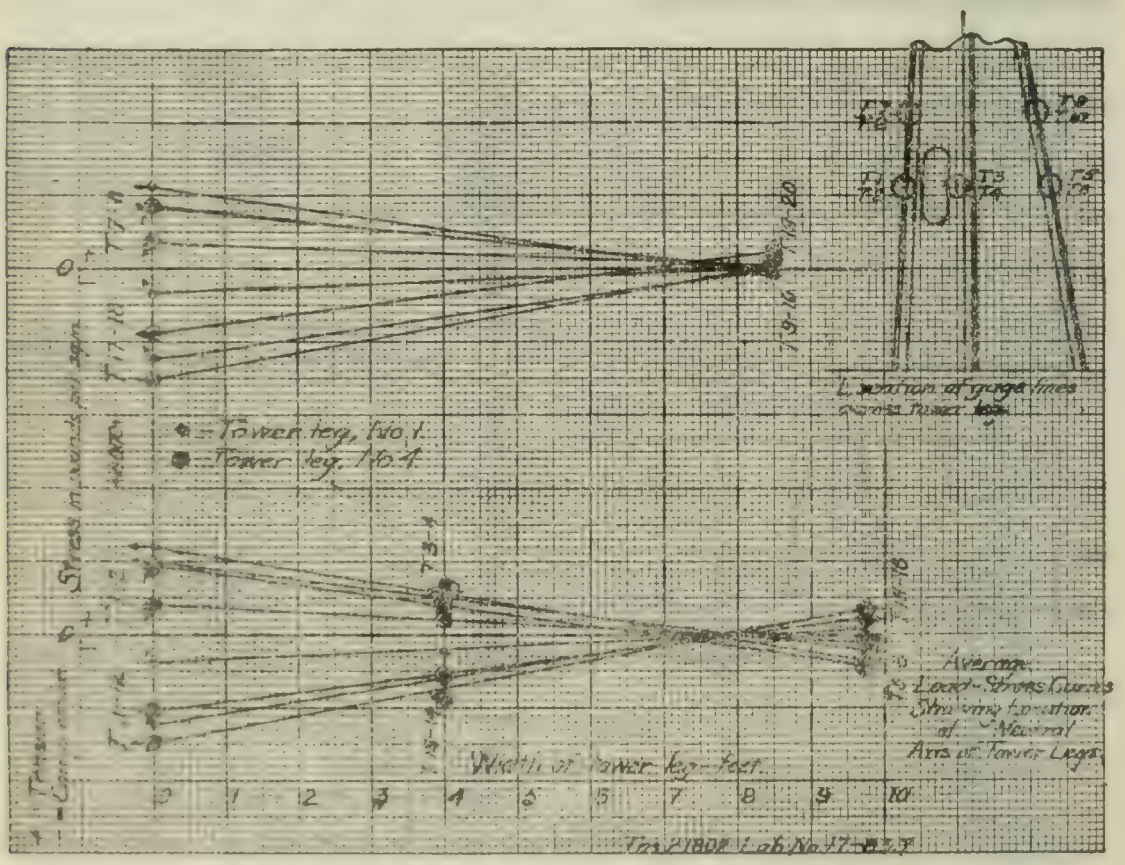



FIG. 13.—*Locations of neutral axes of tower legs*

levers the stresses at opposite sides of the tower might still be equal and opposite, but in this case the neutral axis should be near the middle of the member. The curves show that neither of these but rather some intermediate condition exists, which is probably due to a combination of both actions. The proportion of the total stress due to each of the actions can be roughly determined by the fact that the neutral axis is near the edge of the leg. Considering the upper level of gage lines and assuming that the section of the tower leg is symmetrical about the center line, the tension and compression on opposite sides of the tower leg should be equal. In order to reduce the stress to zero at the inner

edge of the tower, it would therefore be necessary to apply a direct stress equal and opposite to the stress due to the bending. Roughly, then, half of the indicated stress at the outer flange of the tower leg is due to the direct stress of the tower acting as whole and the remaining stress is due to the load carried by the tower leg as a cantilever.

The results of observations taken with the jib abeam are not readily explained. The values obtained for both the 180 and 150 ton loads appear reasonable, but the high stresses indicated for the position of jib up with no load can not be accounted for. Inasmuch as the line of the tower legs on which measurements were taken was at an angle of only 30° with the center line of the pontoon, it was expected that there would be a decrease in the stresses as the jib was rotated from the jib on center line to jib abeam position. It has been shown that with no load and the jib in the upper position, the moment on the tower and therefore the stresses in the tower members were actually negative as compared with the moments and stress produced by loading the jib. The decrease expected in the negative stresses would actually appear as positive stresses, and hence the sign of the stresses produced by rotating the jib to the abeam position are correct, but the magnitude appears unreasonably large. No explanation for this behavior is offered.

*Magnitude of the Stresses in the Tower.*—All the values obtained from the tower gage lines represent positions of the jib within one quadrant of its rotation. It might be assumed that a complete reversal of the jib would cause an equal stress of opposite kind which would result in a range of stress of nearly 50 000 pounds per square inch in some cases. Such a range of stress would clearly be dangerous. Since, however, the zero of the gage lines actually represents a stress of the opposite sign to that resulting from the application of load on the jib, that range of stress caused by rotating the crane will be reduced by twice the amount of the initial stress. It has been shown that the actual stresses should be measured from the 40-ton load line. For the strain gage readings a set of curves showing the stress in the tower plotted against the angle of rotation of the jib from a fixed zero (forward position) point has been plotted for the 180-ton load. These curves are shown on Fig. 14. Although the jib was only rotated through 90° it has been assumed that the readings on the opposite post would represent the stresses obtained by rotating the jib 180°

from each position in which readings were taken. This assumption is justified by the fact that the stresses in corresponding opposite points are equal and opposite in all cases as shown by the average curves. The only questionable part of this procedure is the actual range of stress. It has been shown that this depends primarily upon calculation, for which there is no experimental check except that the calculated load equivalent of lowering the jib, which was based on the same figures, gave a value which agreed closely with the load-stress curves for the individual gage lines.

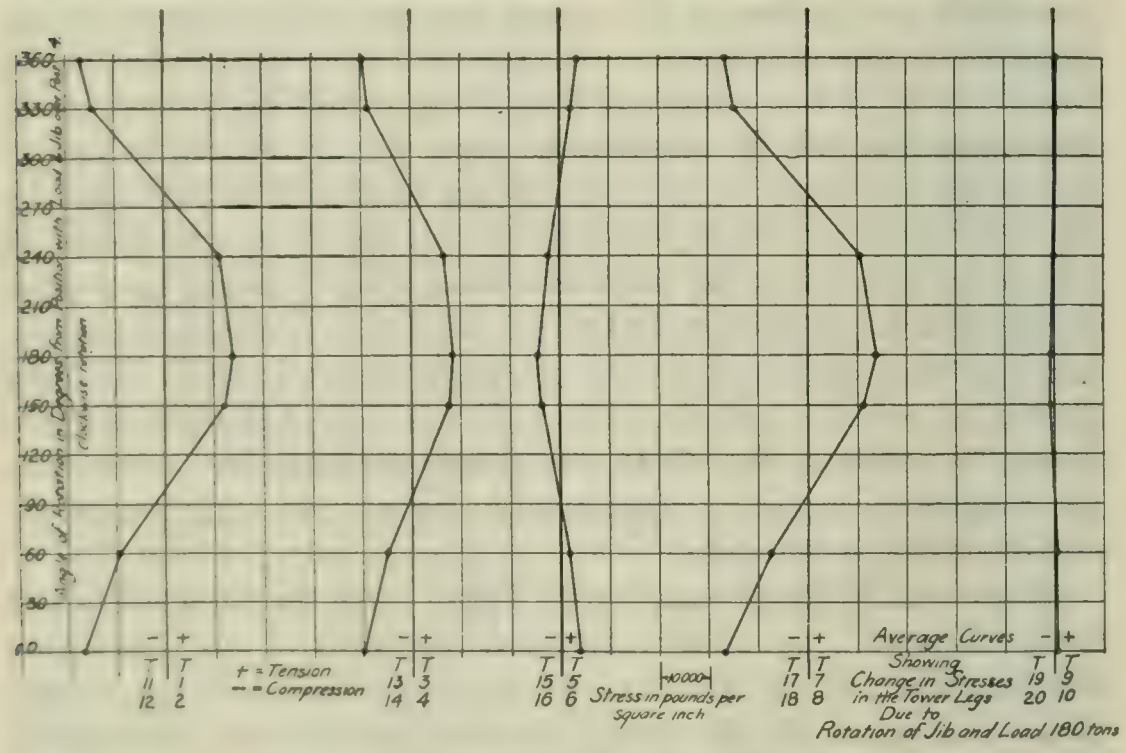



FIG. 14.—*Stress in tower legs under rotating load*

Accepting the calculated values as correct, the stresses vary from 17 000 pounds per square inch in compression to 13 500 pounds per square inch in tension for the 180-ton load. Remembering that the structure with the 180-ton load is carrying an overload of 20 per cent, these stresses may be considered safe.

*Deflection Readings.*—Deflection readings on the tower were taken on tower post No. 4 (see Fig. 15) and are shown graphically on Fig. 16. One curve shows the deflection in the athwartship direction and the other shows the fore-and-aft deflection. Theoretically these should be sine curves having the maximum and minimum values when the jib is in the direction of the deflection measurements and having zero values when the jib is at right angles to this direction. The curves approach these conditions very closely.

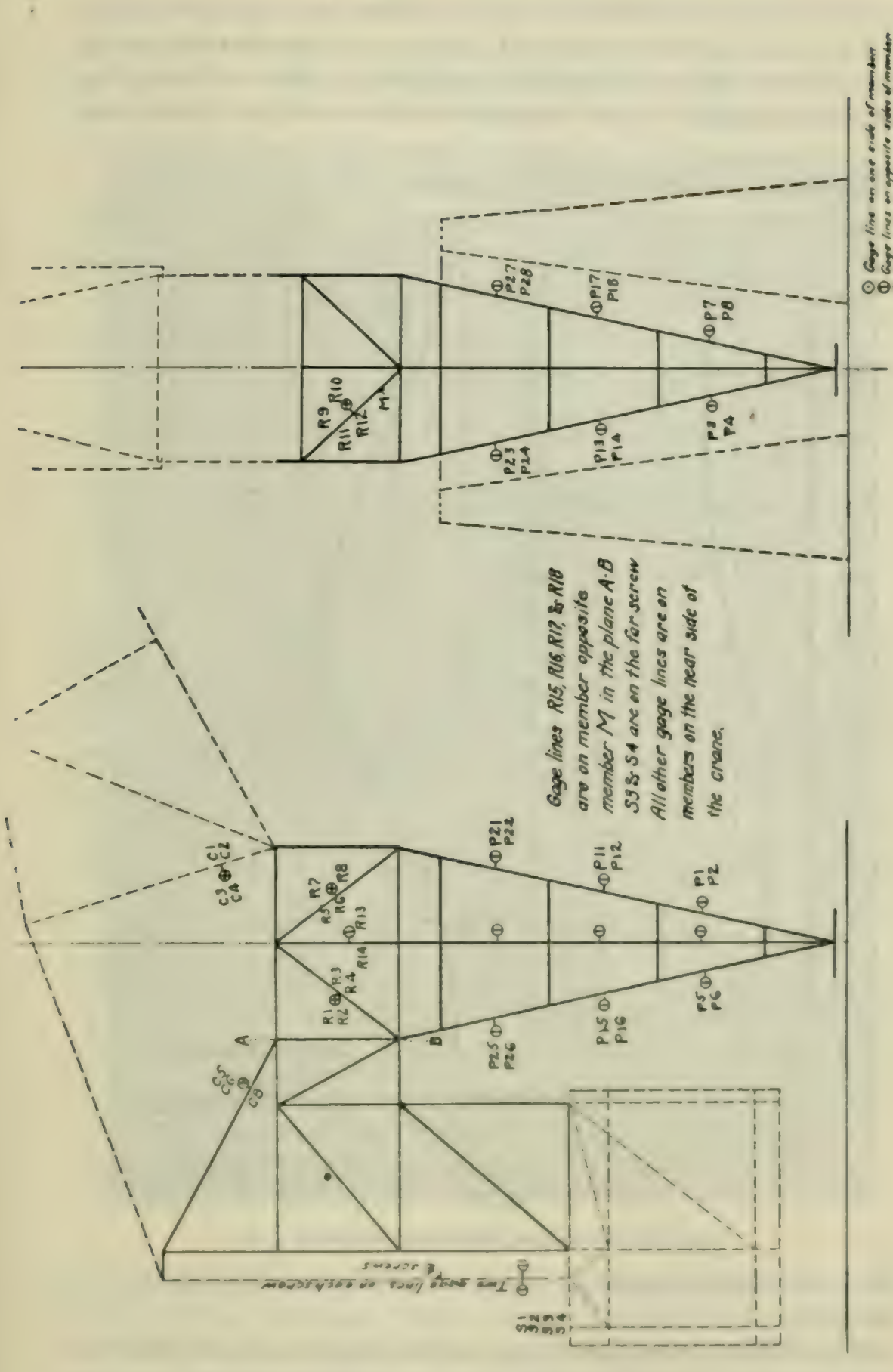



FIG. 15.—*Diagrammatic sketch of 150-ton floating crane pintle and adjacent superstructure, showing location of gage lines*

The fact that the athwart-ship deflection was only about one-half as much as the fore-and-aft deflection, supports the assumption that the tower did not act entirely as a unit. A tower leg acting individually would naturally deflect less in the direction of

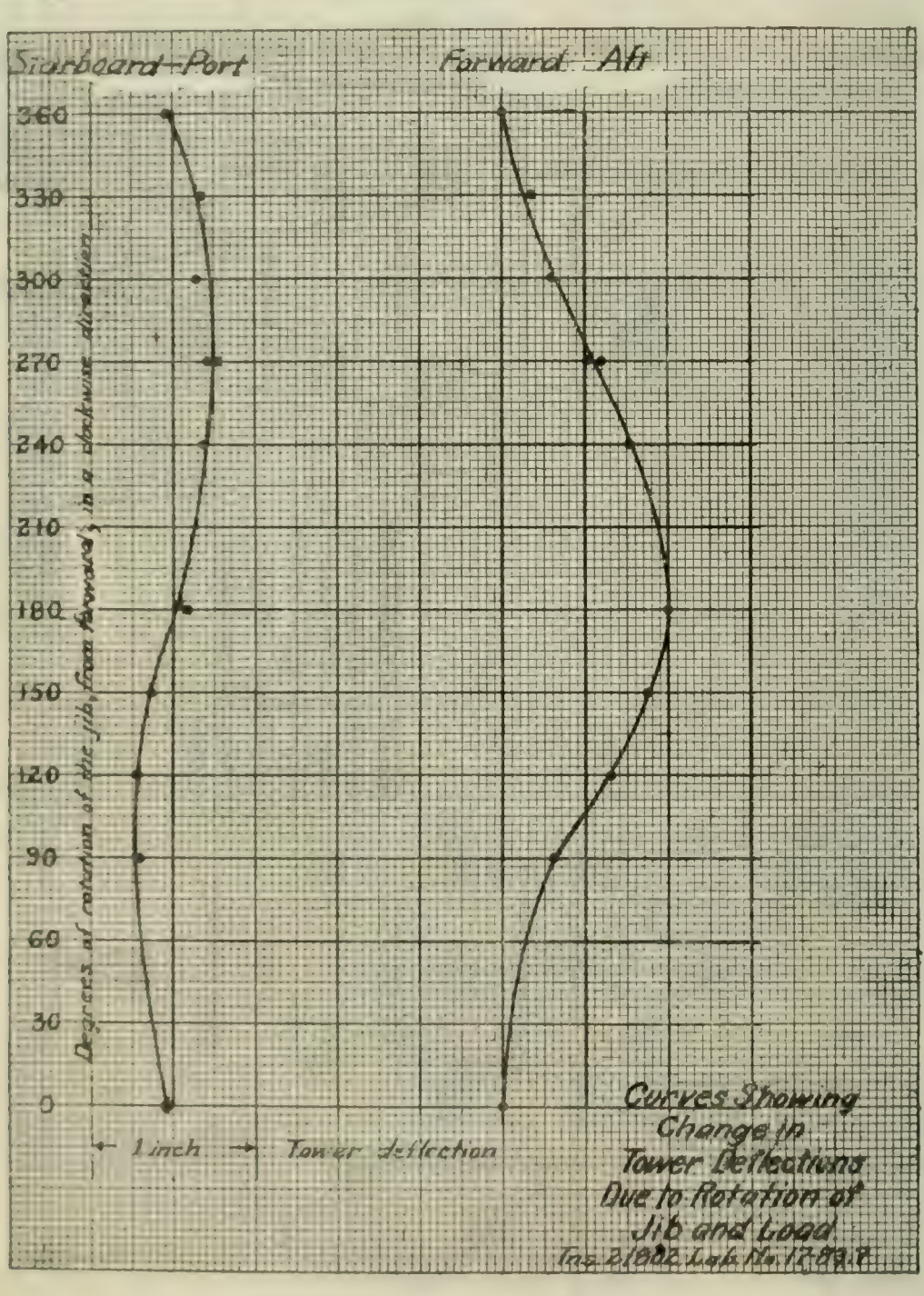



FIG. 16.—*Tower deflections under load*

the larger section modulus, which is the athwart-ship direction in this post.

A maximum deflection of 0.50 inch in the fore-and-aft direction does not appear unreasonably large as compared with 0.25 inch in the athwart-ship direction when it is considered that there is

no post directly fore-and-aft to take the bending in this direction to the best advantage.

(*c*) PINTLE.—The stresses in the pintle are shown on Figs. 17 and 18. It will be recalled that gage lines *P 1*, *P 11*, and *P 21*

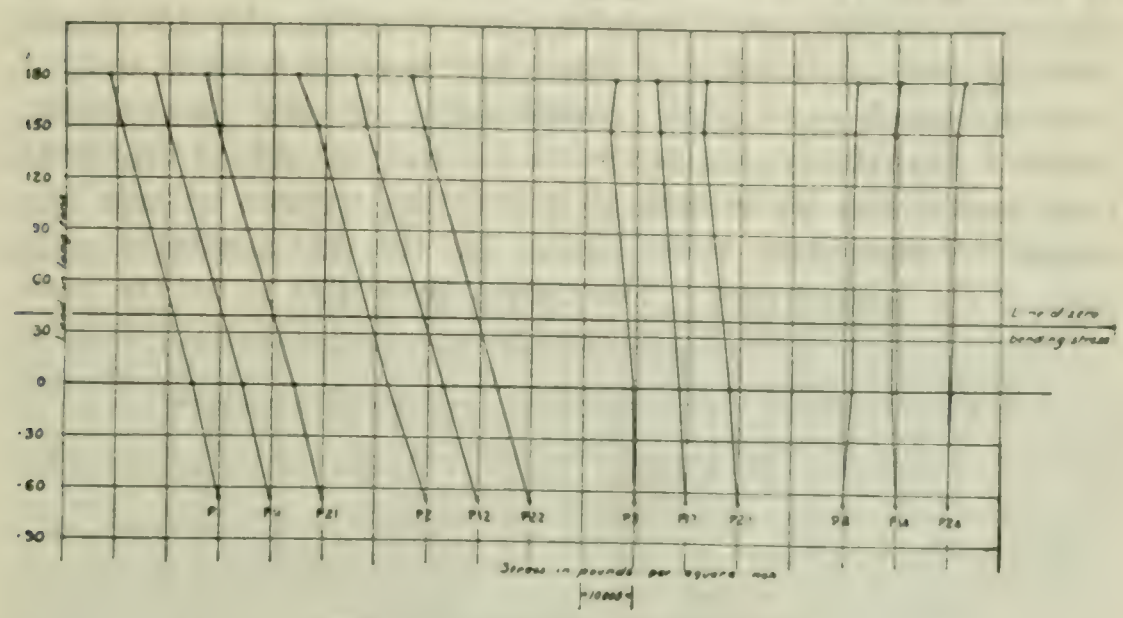


FIG. 17.—*Load-stress curves for pintle*

at the first, second, and third levels, respectively, are on the left side (facing the jib) of the front (No. 1) pintle post. Gage lines *P 2*, *P 12*, and *P 22* are located at the corresponding positions on the right side of the member. The curves are similarly grouped

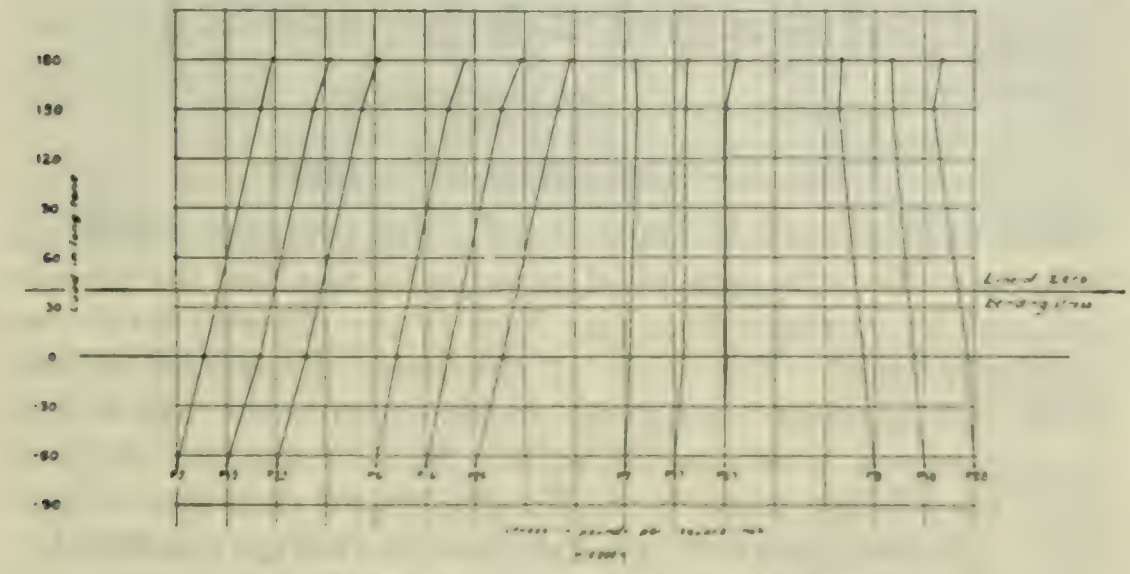


FIG. 18.—*Load-stress curves for pintle*—Continued

for the other pintle posts. A study of these curves shows the stresses to be very nearly equal at the different levels. For the first and the third post there is no consistent difference in the stresses on the two sides of the member. The stress in the first

post is compression in every case, while the third post shows tension at all points. The curves for the second and the fourth post reveal a different condition. Gage lines *P 3*, *P 13*, and *P 23* on the front side of the second post show compression, while the other side of this post is found to be in tension. On the fourth post the odd-numbered gage lines show a small tension and the even-numbered ones show compression. It will be recalled, however, that the even numbers are on the front side of the fourth post, and if the pintle acts as a unit the stresses on this side should correspond to those shown by the odd-numbered gage lines of the second post. The curves show this to be the case.

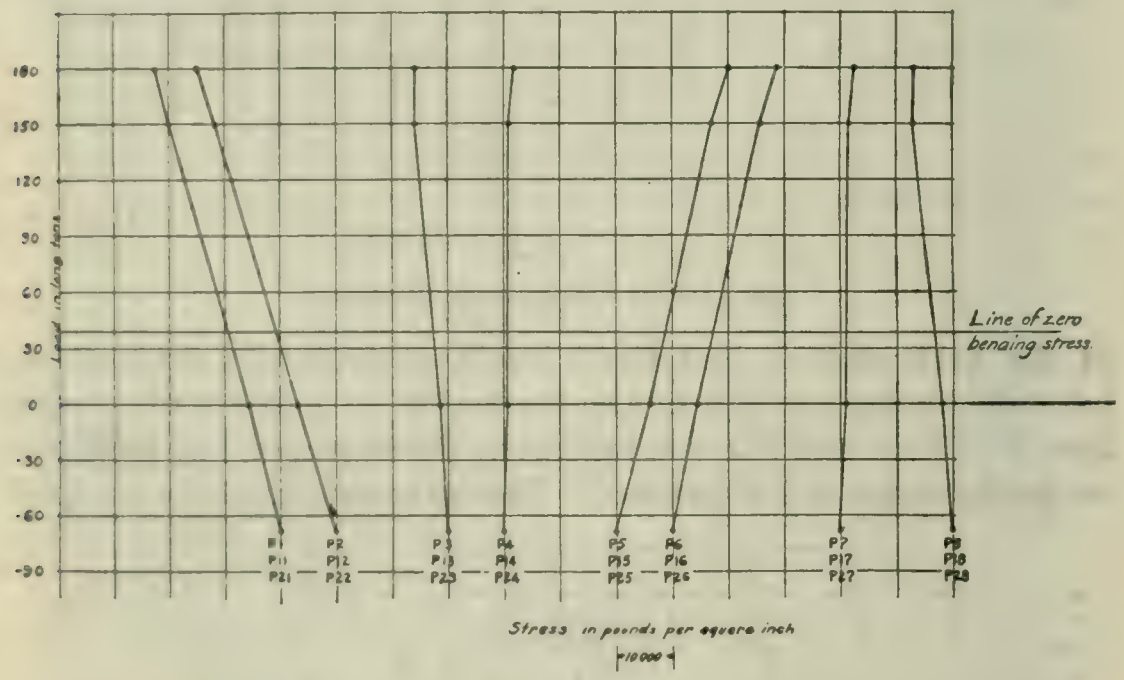



FIG. 19.—*Average load-stress curves for pintle*

*Behavior of the Pintle Under Load.*—The principal conclusion to be drawn from the individual curves is the fact that the stresses indicated by corresponding gage lines at the different levels are practically equal. The study of the stress distribution in the pintle can be more readily accomplished with the aid of the average curves, which are shown on Figs. 19 and 20. Fig. 19 shows the average value of the three levels for each side of each post. The irregularities of the individual curves are considerably reduced by this method of averaging. The left side of the first post (*P 1*, *P 11*, and *P 21*) shows a slightly smaller amount of stress than the right side (*P 2*, *P 12*, and *P 22*) of the same post, the stresses being 22 500 and 25 000 pounds per square inch, respectively. The front side (*P 3*, *P 13*, and *P 23*) of the second post shows a compression stress of 6000 pounds, while the rear

side (*P 4*, *P 14*, and *P 24*) shows a tension of 2000 pounds at the same load.

*Magnitude of the Stresses in the Pintle.*—The rear post (No. 3) shows maximum tensile stresses of 20 000 pounds and 19 000 pounds per square inch on the right and left side, respectively. The fourth post behaves very similarly to the second post, showing a compression of 7000 pounds per square inch on the front side and a tension of 2500 pounds per square inch on the rear side. The compression in the front side and the tension in the rear sides of the side posts (Nos. 2 and 4) are in agree-

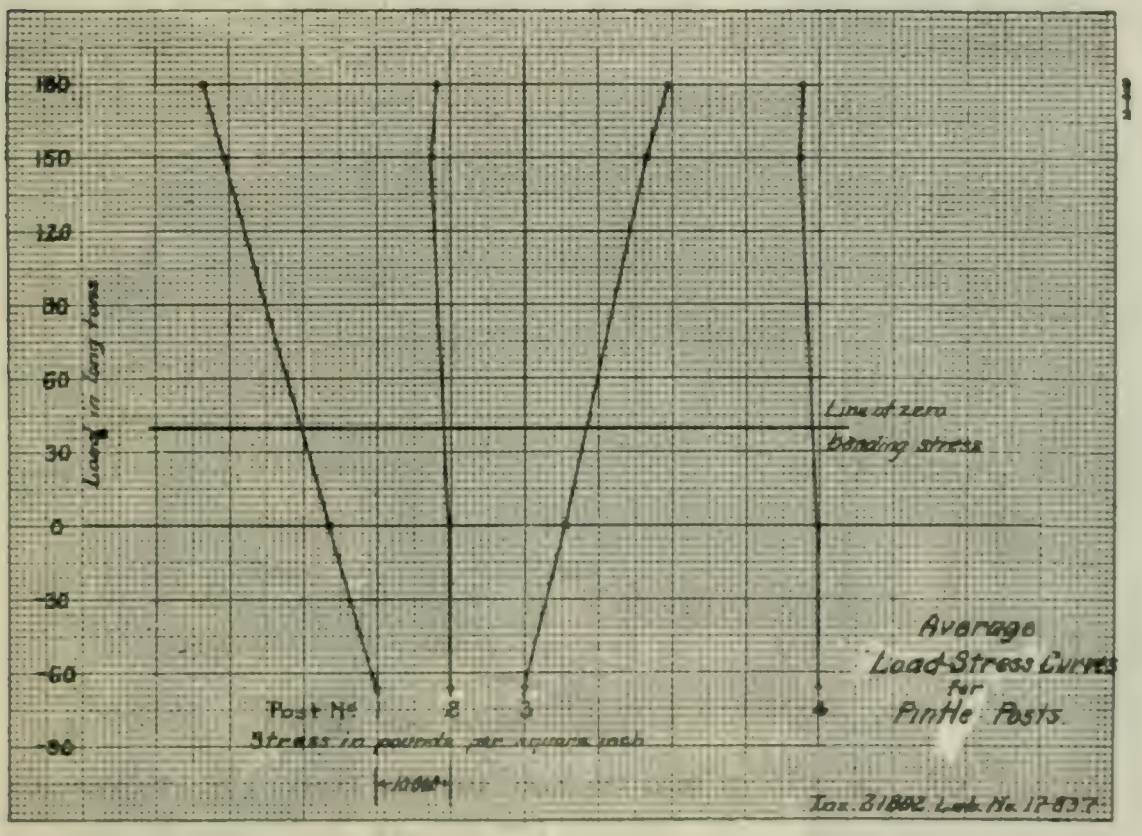



FIG. 20.—*Load-stress curves for pintle posts*

ment with the stresses found in the front and rear posts of the pintle, thus indicating that the pintle acts as a unit with neutral plane passing through the side posts.

Fig. 20 shows the average of all the gage lines of each post.

Curve No. 1 shows a maximum compression of 23 500 pounds; No. 3 a corresponding tension of 19 500, while the side posts Nos. 2 and 4 show a compression of approximately 2000 pounds at the 180-ton load. Considered algebraically, it is seen that if a compression of 2000 pounds per square inch is subtracted from all the values indicated by the curves for the 180-ton load, the compression and tension in the front and rear posts will be equal

and the net result for the side post will be a zero stress. This suggests that the compression of 2000 pounds per square inch was due to the additional weight of 180 tons applied to the pintle.

Just as the range of stress shown for the tower members did not necessarily indicate an actual tension or compression of such an amount, so also the range of stress shown for the front and rear pintle post may be divided into tension and compression. Measuring the stresses from the 40-ton load line results in an indicated compressive stress of 13 000 pounds per square inch in the forward post (No. 1), and an indicated tensile stress of 11 000 pounds per square inch in the rear post (No. 3), under the 180-ton

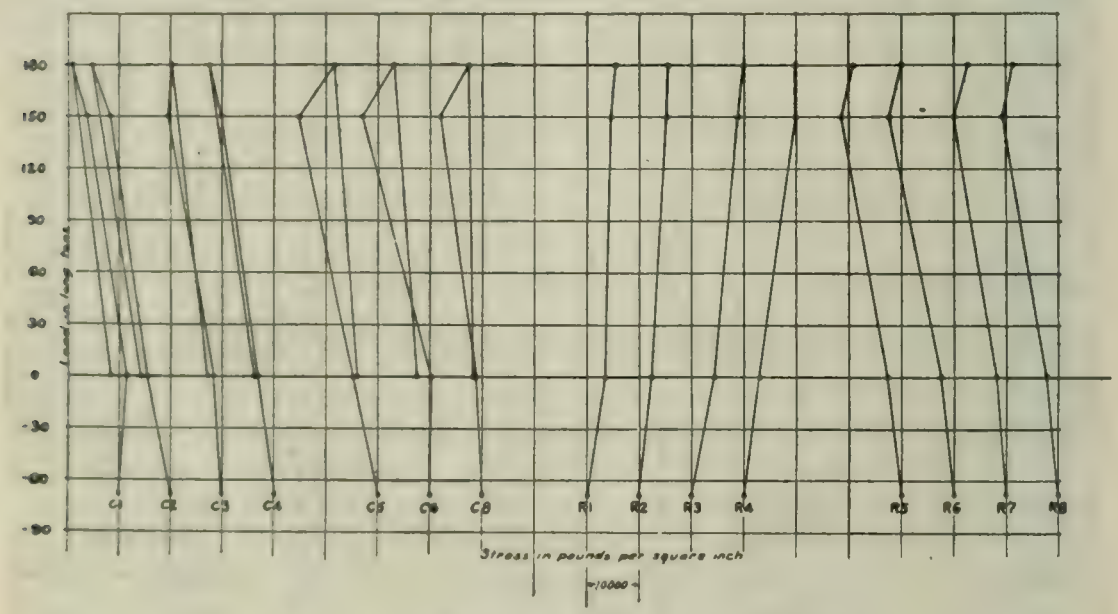



FIG. 22.—*Load-stress curves for superstructure*

load. With the jib up and no load on the hook, the stresses are 10 500 tensile and 8500 pounds per square inch compression on the front and rear posts, respectively.

The direct stress due to dead and live load is approximately 5000 pounds per square inch compression. This stress must be added, algebraically, to the above values, due to bending, which results in a maximum compressive stress of 18 000 pounds per square inch in the front post and 13 500 pounds per square inch in the rear post. This is not excessive for a structure under 20 per cent overload. The maximum tensile stresses are only 6000 and 5500 pounds per square inch on the front and rear posts, respectively.

*(d) Superstructure.*—The locations of the gage lines on the superstructure are shown on Fig. 15. The load-stress curves for the individual gage lines will be found in Figs. 22 and 23. Al-

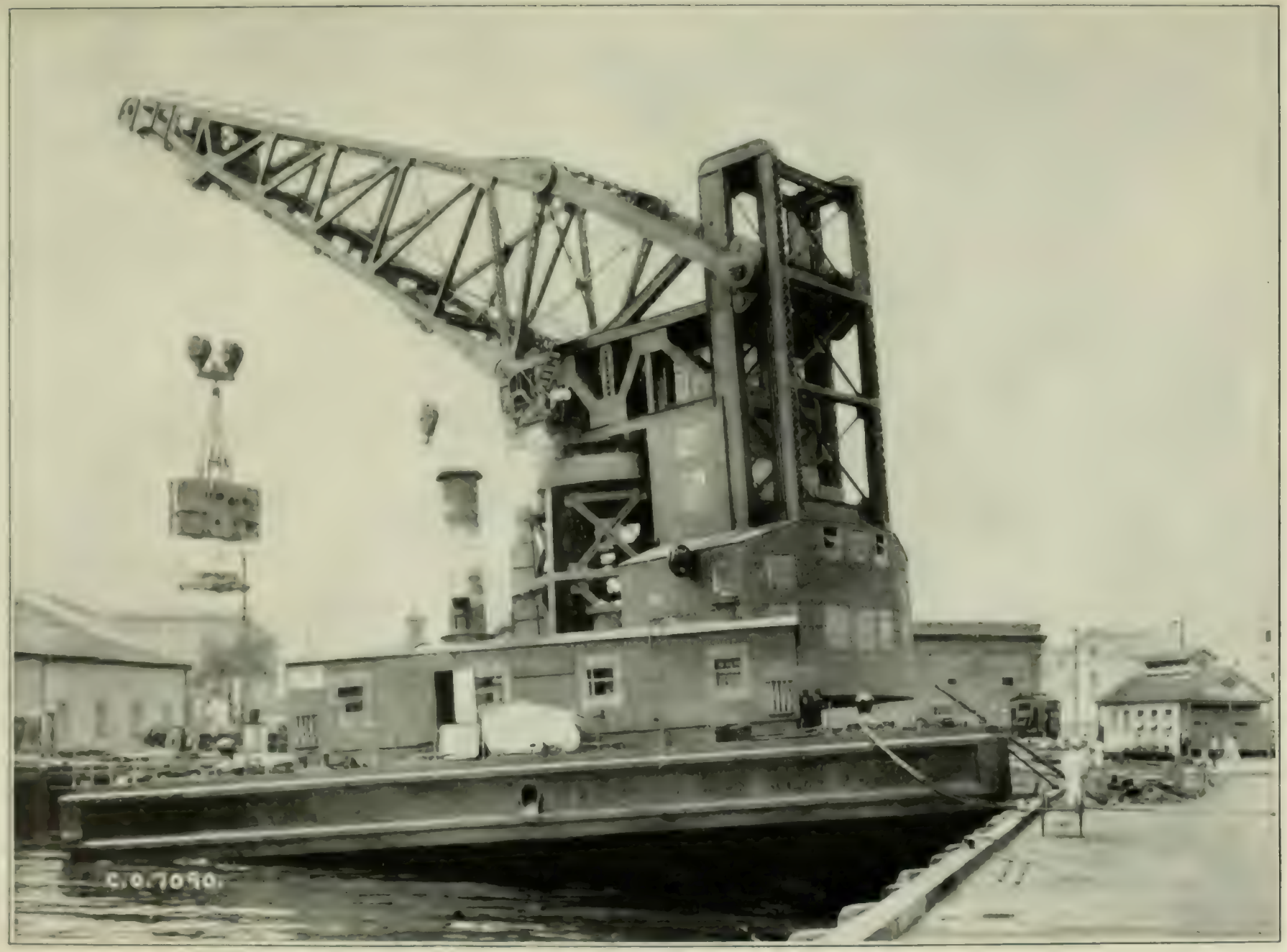


FIG. 21.—*Crane under load of 180 tons, load swung to port*

though several of the groups of curves do not show a straight-line relation of load to stress, still it will be seen that the curves in each group are quite similar and in most cases nearly parallel. Any bending in the members would result in a non-uniform stress distribution across the section giving curves which are not parallel.

*Vertical Posts of the Superstructure.*—The most noticeable bending is shown by gage lines *R 13* and *R 14* on the vertical post of the side truss of the superstructure. The rear side (*R 14*) of this member is found to be in compression while the front side shows a slight tension. This would indicate that the member was bending with the concave side toward *R 14*. An examination of the stresses in the adjacent members reveals that both diagonals

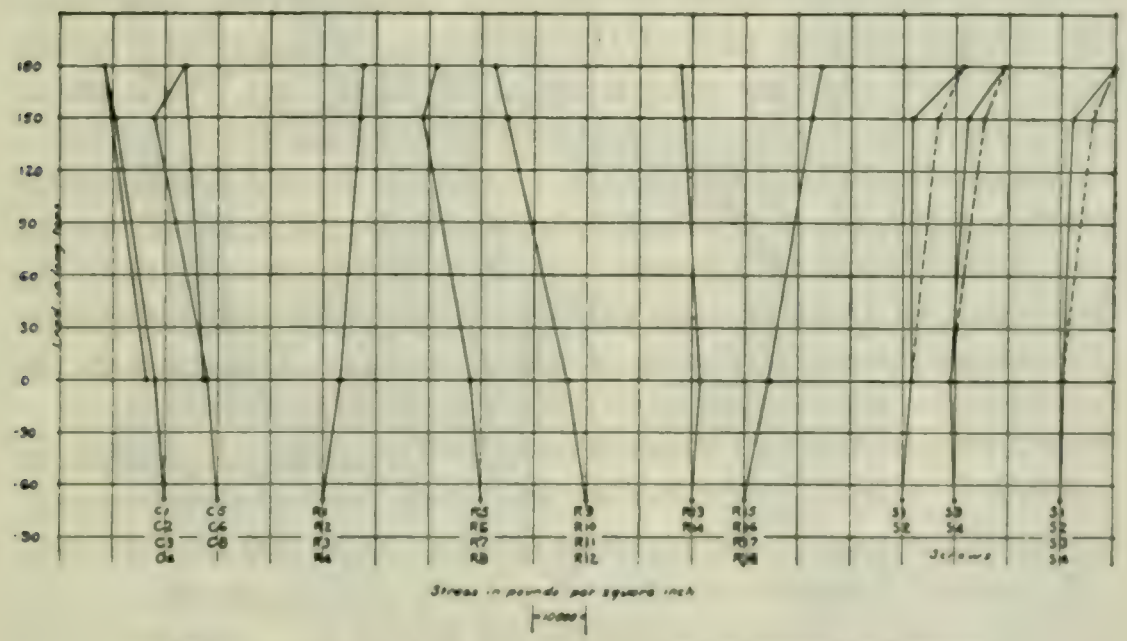


FIG. 23.—*Average load-stress curves for superstructure and screws*

framing into the top of the post exert forces toward the rear of the superstructure. These would naturally cause a bending in the post in the direction indicated by the readings, provided this post was somewhat fixed at the bottom, a very logical assumption for a riveted member.

The behavior of the structure under load is more evident from the average curves for the various members. These are shown on Fig. 23.

*Jib Members.*—The stress in jib members (*C 1*, *C 2*, *C 3*, and *C 4*) is nearly proportional to the load applied to the jib, attaining a maximum value of only 12 000 pounds per square inch. The discrepancy in the two readings at the zero load may be partially due to a slight difference in the height to which the jib was luffed when these readings were taken.

*Struts for the Luffing Screw Guides.*—The behavior of the compression strut supporting the guides for the luffing screws is apparently very erratic, the stress caused by the 150-ton load being 12 000 pounds per square inch while the 180-ton load produces a compression of only 6000 pounds. From the drawings of the structure it will be seen that the horizontal component of the tension in the links which support the jib produces no effect in the strut under discussion except when the jib is near its lower position. In lowering the jib after this position is reached, at which the strut commences to take a portion of the link load, the load carried by the strut varies rapidly with a small change in the position of the jib. It will be recalled also that the position of the jib was determined by the clear reach of the crane hooks beyond the side or end of the pontoon. The amount of list must increase with the magnitude of the hook load. It is therefore evident that with a load of 180 tons the jib would be luffed to a higher position than for the 150-ton load, and consequently a smaller portion of the link load would be transmitted to the compression strut in question. It is quite conceivable that the proportion of the link load carried by the strut was sufficiently reduced by the slight raising of the jib to make the stress in the strut less for the 180-ton than for the 150-ton load.

*Side Diagonals of the Superstructure.*—The diagonal member on which *R 1*, *R 2*, *R 3*, and *R 4* were located, shows a stress proportional to the load. The stress is tension, as would be expected, and reached a maximum of 7000 pounds per square inch. The next curve for gage lines (*R 5*, *R 6*, *R 7*, and *R 8*) represents the stresses obtained in the front or first diagonal of the side truss. The behavior of this member is not readily explained and is in fact contrary to expectations. Aside from the fact that the stress is not entirely proportional to the load, it is found that the stress in the member is compression, instead of tension, as had been anticipated. Apparently the only plausible explanation for this is that the horizontal reaction on the front pintle post is carried by beam action in the lower chord of the end truss to the side trusses, thus producing a compression in the lower chords and the end diagonals of these trusses. If the compression thus produced in the diagonals is greater than the tension produced by the load transmitted through the vertical corner posts, the resulting stress in the member would be compression as indicated. It is impossible to state definitely the way in which the loads are carried by this complicated, indeterminate structure, without

FIG. 24.—*Crane under load of 150 tons, load swung to starboard.*

stress measurements on some of the other members, such as the lower chords of the trusses and the front corner posts.

*Front Diagonals of the Superstructure.*—The stress in the diagonal of the front truss is shown by the average curves for gage lines *R 9*, *R 10*, *R 11*, and *R 12*. A maximum compressive stress of 17 000 pounds per square inch is indicated. The vertical post, on which gage lines *R 13* and *R 14* were located, apparently carried a very small load in direct stress, the maximum average compression being only about 2000 pounds per square inch. As has been previously stated, this member was subject to considerable bending, which resulted in a fiber stress of about 7000 pounds per square inch at gage line *R 14*. The extreme fiber,

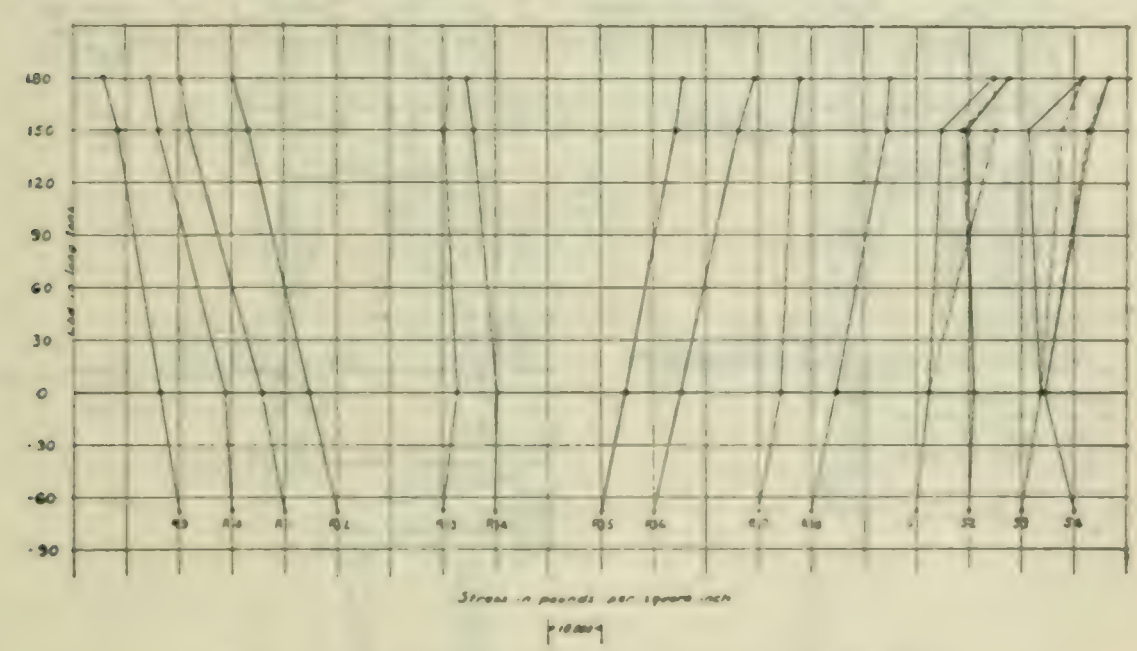



FIG. 25.—*Load-stress curves for superstructure and screws*

which was considerably farther from the neutral axis than gage line *R 14*, was undoubtedly more highly stressed than 7000 pounds per square inch.

The stress in the diagonal of the truss, which frames into the rear pintle post, is shown by the average curve of *R 15*, *R 16*, *R 17*, and *R 18*, and amounts to 14 000 pounds per square inch in tension. From the framing of the structure it would appear that the stresses in the diagonals of the end trusses should depend upon the stress in the front and rear pintle posts. It is found that the ratio of the stress in the diagonal to stress in the corresponding pintle post is almost exactly the same for the diagonals in the front and rear trusses.

(*c*) SCREWS.—The results of the observations on the screws shown in Fig. 25 indicate a peculiar behavior. Considering the

portion of the curve above the zero line it would be expected that the stress should increase approximately with the load applied at the hook of the jib when the jib is in practically the same position. Two sets of readings are shown for the 150-ton load, the full-lined curves showing the first set and the dotted line the second set. The individual curves for either set are very irregular,

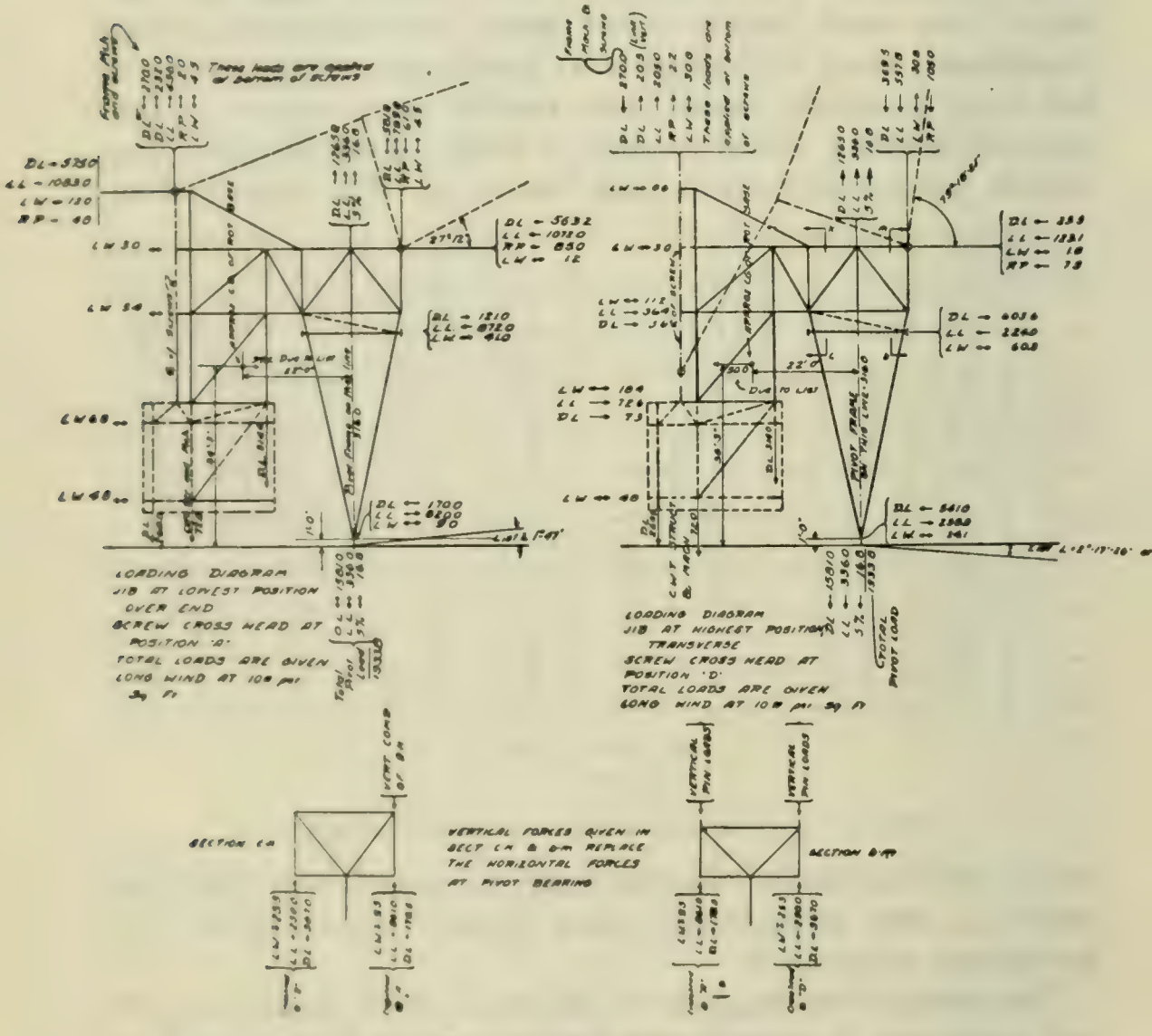



FIG. 26.—*Stress sheet of crane.*

and in some cases the indicated stress is less for the 150-ton load than for the zero load, while others show a large increase in stress over this same range. The large difference in the stress observed on the opposite sides of the same screw must be due to bending in the screws.

The average for each screw and the average of both screws are shown on Fig. 23. The behavior of the two screws is seen to be

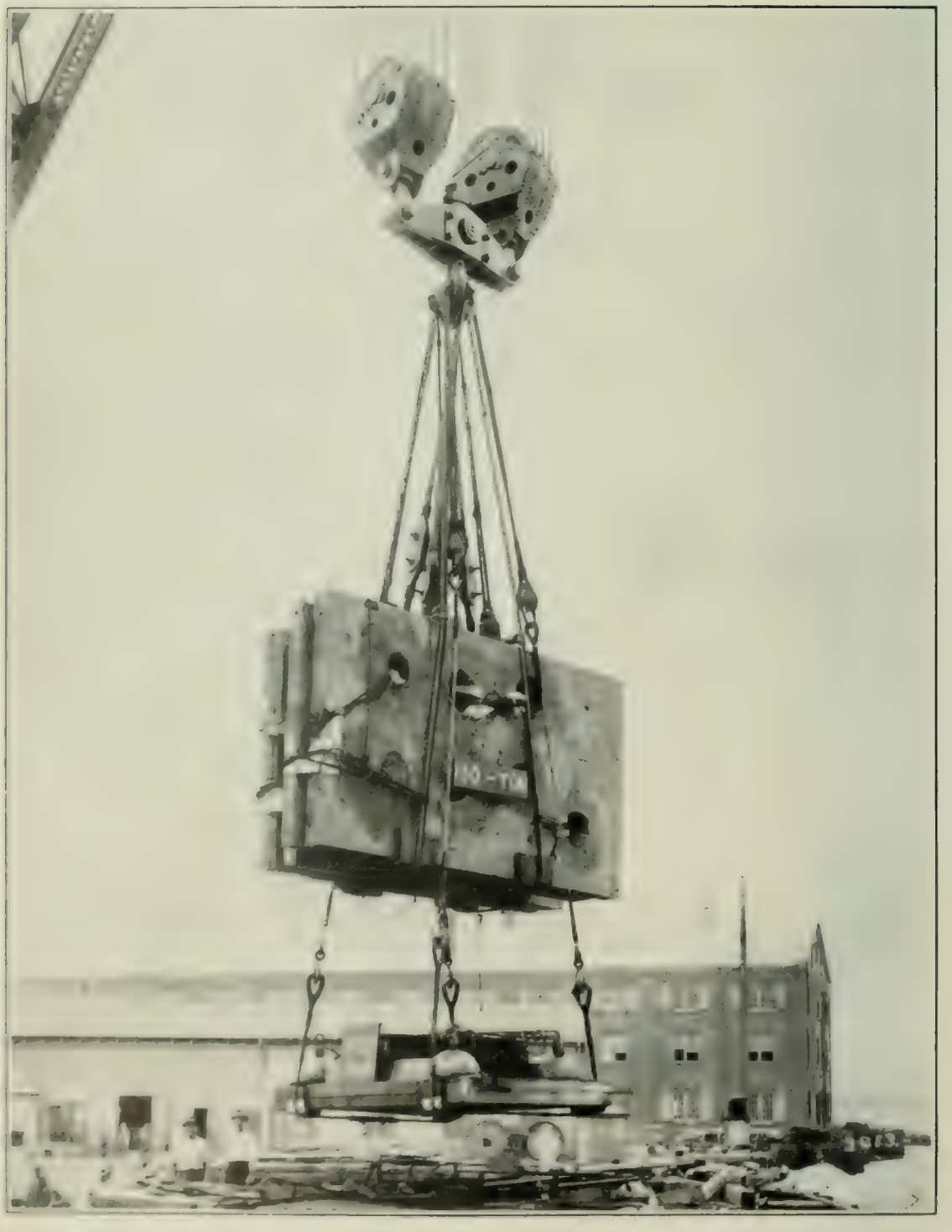


FIG. 27.—*Weights forming load at 180 tons.*

very similar. The stress at the 150-ton load is apparently low, and it will be noted that the second set of readings gives much more reasonable looking results than the first set. From this it might be concluded that the friction on the guides carried a portion of the vertical load for a time, but that by the time the second set of readings was taken the load had been released to screws. It should also be noted that the jib was luffed up or down at each load until the proper reach was attained. It is therefore impossible to state in which direction the jib had been last luffed before the readings were taken. The direction of luffing would greatly affect the stresses in the screws, if the friction on the guides was appreciable.

## IV. SUMMARY AND SUGGESTIONS

### 1. SUMMARY

1. Although the test conditions were not ideal, the consistency of the results is sufficient evidence that in general they are dependable.

2. The stresses in the deck of the pontoon are very small under any of the conditions of load and position of the jib investigated.

3. The range of stress in the outer edges of the tower legs for the 180-ton load is from 17 000 pounds per square inch in compression to 13 500 pounds per square inch in tension.

4. The maximum compressive stresses, including the dead load, in the front and the rear pintle posts are 18 000 and 13 500 pounds per square inch, respectively, for the 180-ton load.

5. The stresses in the superstructure are not excessive unless the dead-load stresses are high.

6. The indicated stresses in the screws are rather uncertain but apparently not excessive.

### 2. SUGGESTIONS

Should more accurate and detailed information on the behavior of such a structure be desired, the following suggestions should prove valuable:

1. The strain-gage observations should, if possible, be made at night or on cloudy days unless it is practicable to shade the entire structure. Standards bars should also be used.

2. The true zero for the stresses in the tower should be determined either by taking readings with the jib in two positions

180° apart or by balancing the counterweight with a live load on the hook.

The stresses for zero bending in the pintle should be determined by balancing, as suggested above.

3. The stress distribution in the superstructure should be determined by observations on all the principal members instead of the few that were used in this test.

WASHINGTON, June 19,1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 152

## INVESTIGATION OF THE COMPRESSIVE STRENGTH OF SPRUCE STRUTS OF RECTANGULAR CROSS SECTION AND THE DERIVATION OF FORMULAS SUITABLE FOR USE IN AIRPLANE DESIGN

BY

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By James E. Boyd

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Arrangement of compression tests | 4 |
| 1. Test pieces | 4 |
| 2. Compression measurements | 4 |
| 3. Deflection measurements | 5 |
| 4. Testing machines | 5 |
| 5. Adjustment in the machine | 5 |
| 6. Counterweights | 5 |
| III. Square-end struts | 6 |
| 1. Experimental results | 6 |
| 2. Test of formulas | 9 |
| 3. Rankine's formula for square-end struts | 12 |
| IV. Cross-bend tests | 14 |
| 1. Experimental results | 14 |
| 2. Discussion of results | 16 |
| V. Round-end struts | 17 |
| 1. Experimental results | 17 |
| 2. Test of formulas | 19 |
| VI. Conclusions | 23 |
| VII. Theory of certain tapered struts | 24 |
| 1. Shape of strut | 24 |
| 2. Derivation of formulas | 25 |
| 3. Application of formulas | 26 |
| 4. Approximate calculations | 32 |
| 5. Relation of the strength of a strut to its stiffness as a beam | 33 |


## I. INTRODUCTION

These experiments were undertaken for the purpose of finding suitable formulas and constants for the design of spruce struts for airplanes. Test specimens of rectangular cross section (approximately square) were used, as these sections are easy to prepare and the necessary calculations are easily made. The constants and formulas which have been obtained apply to stream-line or

other sections, provided they are uniform throughout their length. The constants apply to struts of tapering section, and the formulas may also be applied, provided a moment of inertia is used which is somewhat less than that of the maximum section. Theoretical methods of computing the strength of tapered struts are given in the last pages of the paper.

The experimental work was conducted under the general direction of Prof. John H. Nelson, engineer physicist of the Bureau of Standards, who decided upon many of the methods employed. C. P. Hoffman and L. J. Larson assisted in making the measurements. The curves and drawings were finished by Prof. C. L. Svensen, of the Ohio State University. Prof. R. D. Bohannan made some suggestions in connection with the theoretical work.

## II. ARRANGEMENT OF COMPRESSION TESTS

### 1. TEST PIECES

In the preparation of the struts, one edge of the plank was first straightened on a jointer. A strip a little over 1.75 inches square was cut off with a saw and planed to size. Each plank furnished five strips designated as A, B, C, D, and E, in order, and also a narrow strip from which endurance test pieces were taken.

The planed strips were cut to length with a back saw and the ends finished by grinding on an emery wheel mounted in a lathe. The strut was held in position perpendicular to the plane of the emery wheel by a pair of right-angled V guides mounted on the bed. These guides were about 2 feet apart when used with the longer struts, so that the end was perpendicular to the last 2 feet of the strut and not perpendicular to its entire length in those cases in which the strut was not perfectly straight.

### 2. COMPRESSION MEASUREMENTS

For the two shorter lengths the compression was measured by means of a pair of Berry strain gages. For all other lengths a pair of 30-inch Howard gages were used.

To support the gages, a pair of steel pins, each 0.237 inch in diameter, were driven through holes drilled in the strut at the ends of the gage length, these holes being slightly smaller than the pins to give a driving fit. The struts were tested in a horizontal position, with the steel pins also horizontal.

The conical points of the strain gages rested in small holes drilled in the upper surface of the pin. The holes were 2.75 inches apart, which placed the gage points one-half inch from the

vertical surface of the strut. The strain gages were held firmly in place by means of 3-pound weights suspended from stirrups which were attached to the gages directly above the points.

### 3. DEFLECTION MEASUREMENTS

The deflection of the two shorter lengths of the square-end struts was measured by means of a pair of Ames dials mounted in a metal yoke which was supported by the base of the testing machine. The vertical deflection of the two shorter lengths of round-end struts was measured by an Ames dial supported by a wooden beam which rested on a pair of clamps attached to the strut near the ends.

For all other lengths a pair of Johnson dials were used.

### 4. TESTING MACHINES

The two shorter lengths of square-end struts were tested on the 230 000-pound Emery machine, and all the others in the 2 300 000-pound Emery machine.

Both these Emery machines at the Bureau of Standards are of the horizontal type.

### 5. ADJUSTMENT IN THE MACHINE

One end of the strut was placed squarely against one head of the Emery machine, and a light load applied, after which the adjustable head was rotated until an even bearing was secured at the other end. This position of best bearing was determined by means of a Starrett gage of thin sheet metal inserted between the strut and the head. It was also tested by observation of the load on the strut as given by the reading of the balance beam of the testing machine. The position of the head giving the least load is the one required.

For the longer struts it was found advisable to fix the heads nearly parallel, but slightly wider apart at the top than at the bottom. In the case of a strut which was not initially straight, a light load (200 to 300 pounds) was found sufficient to bring it to full bearing and make it more nearly straight than it was before loading.

### 6. COUNTERWEIGHTS

Each Howard gage with 30-inch rod weighs 3 pounds. With a 3-pound weight on each end, the total weight of the two gages is 18 pounds. This load caused considerable deflection of the longer struts. Nine-pound weights, fastened to strings passing

over light pulleys, were attached to the strut at each gage point to counterbalance the weight of these instruments. Counterweights were not used with the two short lengths of round-end struts, nor with the three short lengths of square-end struts. The weight of the strut itself was not counterbalanced. Struts with initial bend in the vertical plane were placed in the machine convex upward, so that their weight tended to straighten them. For a few struts with relatively large initial deflection upward the counterweights were reduced.

## III. SQUARE-END STRUTS

### 1. EXPERIMENTAL RESULTS

The struts for the square-end tests were taken from six 12-foot planks. There were 10 lengths, from 12⅝ inches, for which $\frac{L}{r}$ is 25, to 10 feet 6¼ inches, for which $\frac{L}{r}$ is 250. The planks were numbered from 1 to 6. The schedule was so arranged that, with a few exceptions (made necessary in order to reserve one piece of each plank for a bending test), one strut of each length was taken from each plank. The complete schedule of struts is given in Table 3.

Most of the struts of the two shorter lengths failed by compression at the transverse pins which supported the gages. This seemed to indicate that a cylindrical pin with higher modulus of elasticity than the material which surrounds it was a source of weakness in a compression member. To investigate this question two 12⅝-inch struts, C–5 and E–6, were tested with gages supported by clamps instead of pins. Each failed at a lower load than the strut from the same plank which had been tested with the pins. If any conclusion may be drawn from these few tests, it is that the pins do not seriously weaken the strut.

The summary of the data for the eight struts of 12⅝-inch length is given in Table 3.

Table 1 gives the complete data of the test of square-end strut B–4, 4 feet 2½ inches in length, for which $\frac{L}{r}$ is 100. Columns II and V give the compression at the north and south gages, respectively. The load was somewhat eccentric, so that the reading at the north gage is considerably larger than at the south gage. The gages were 2.75 inches apart, while the width of the strut was a little under 1.75 inches. The actual difference of compression at the faces of the strut is seven-elevenths of the difference of the

gage readings. To get column III, subtract two-elevenths of the difference of the readings of columns II and V from the reading of column II. To get column VI, add the same amount to the the readings of column V. Column IV gives the unit compression in the north face of the strut, and column VII gives the same for the south face. Column VIII gives the average unit compression.

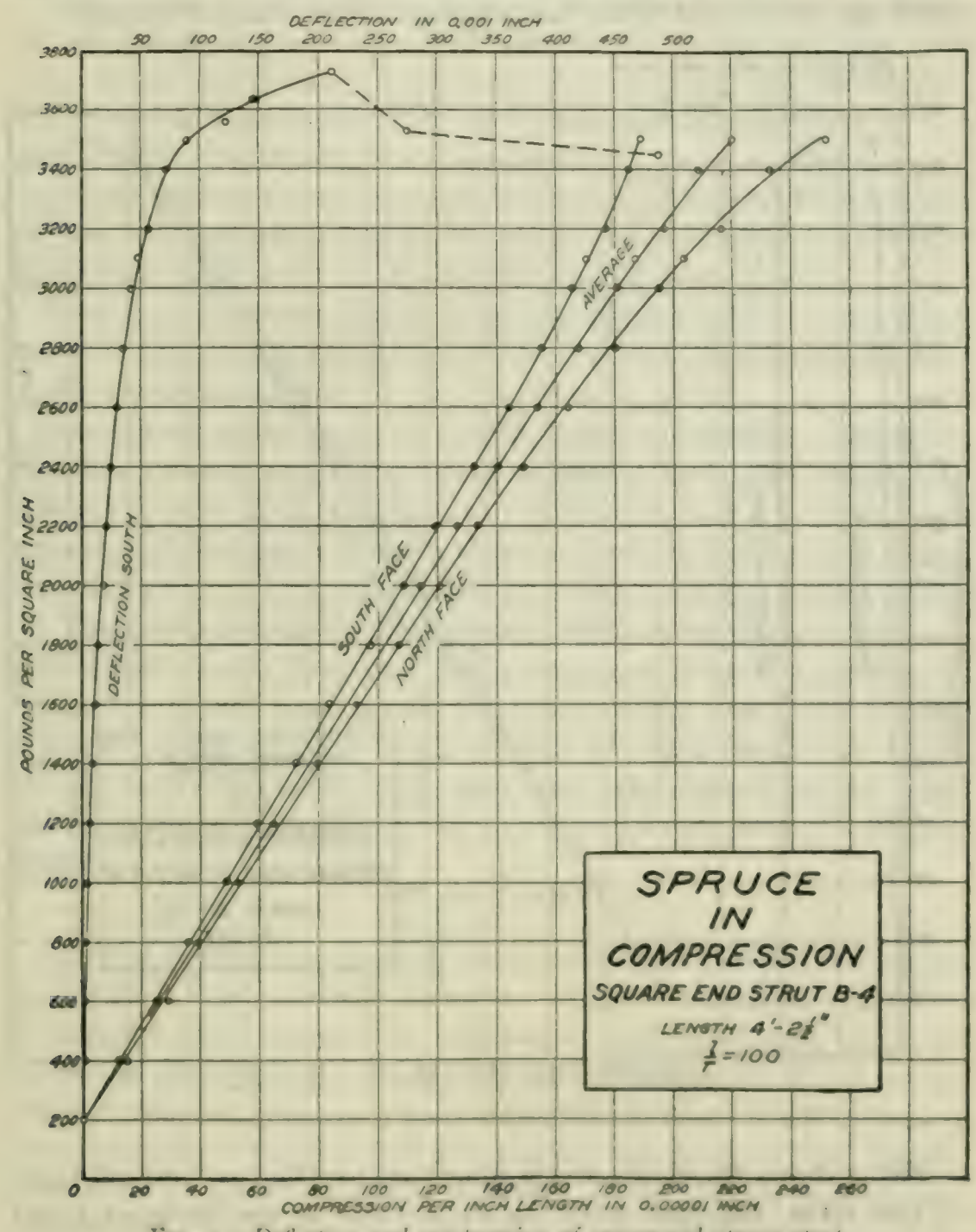


FIG. 1.—*Deflection and compression of square-end spruce strut*

Fig. 1 shows the stress-strain diagrams for this strut, together with the deflection in the horizontal plane. The greater compression is in the north face, which is the concave side when the deflection is south.

Table 2 gives similar data for a second strut, C–4, of length 5 feet $3\frac{1}{8}$ inches, for which the slenderness ratio is approximately 125. In this case the horizontal eccentricity was small, so that the readings of the two instruments are nearly equal. The readings of the north gage are the larger until the last load is reached, when that of the south gage becomes the larger. At the same time the horizontal deflection changes from south to north.

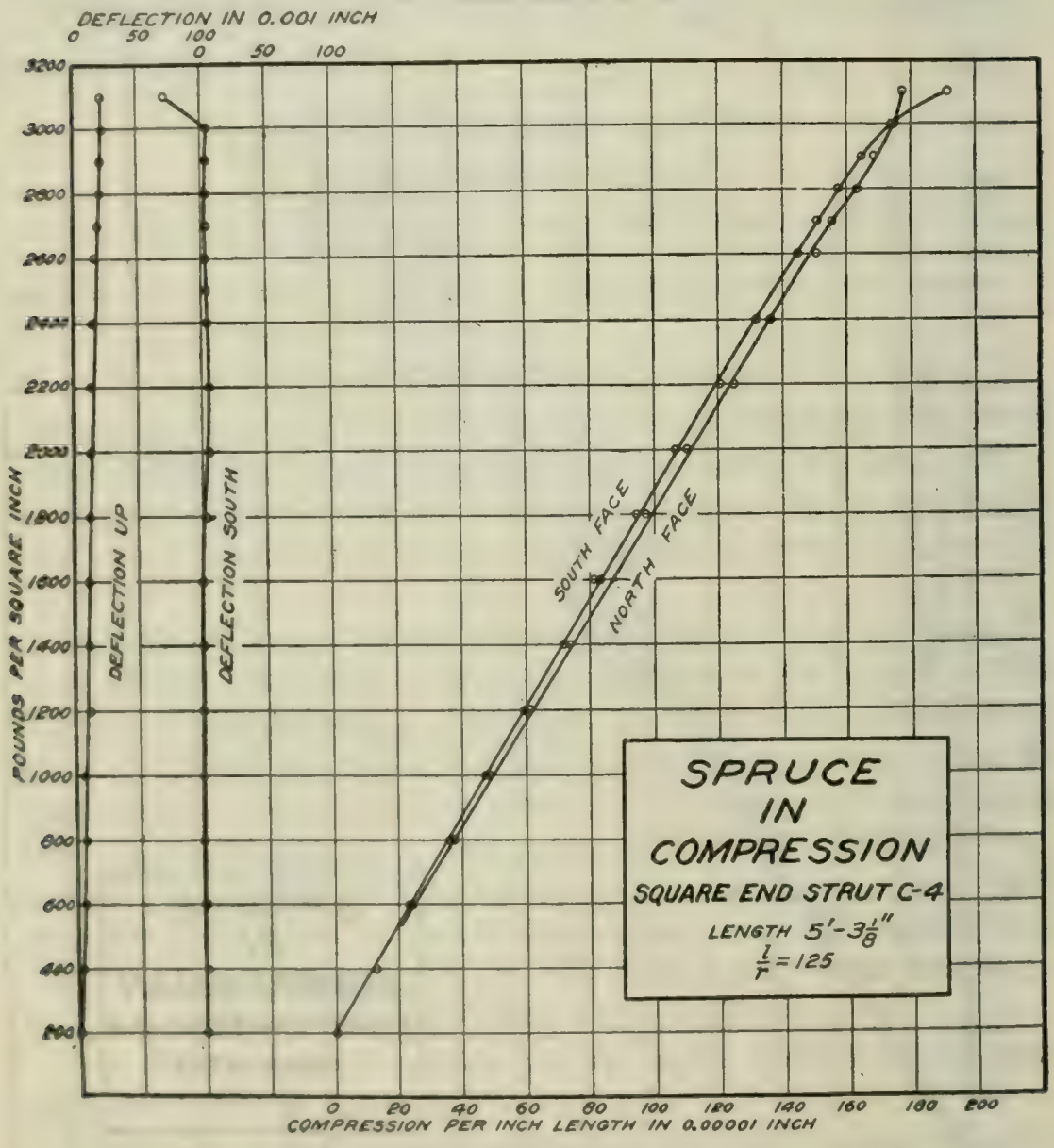


FIG. 2.—*Deflection and compression of square-end spruce strut*

Fig. 2 shows the stress-strain diagrams for the two vertical faces of this strut, together with the deflections in the horizontal and the vertical planes.

Tables 1 and 2 and Figs. 1 and 2 are representative cases of the tests of square-end struts. Generally the longer struts were not carried to compression failure. When the deflection reached about

0.875 inch, so that the center of the section at the middle of the length was in line with the edges of the sections at the ends, the strut rotated on the edges at the ends and came into the condition of a round-end column. The load for this condition was much reduced, and with continued compression the load became still smaller.

Fig. 3 shows the unit load and the average unit compression for all the square-end struts of slenderness ratios 100, 150, and 200. The broken-line extensions of some of the curves are carried up to the ultimate unit loads as found after the removal of the gages which measured the compression. These extensions give the true ultimate load, but not necessarily the real form of the curves. The straight-line part of each curve is extended upward to a convenient point for finding the modulus of elasticity.

Similar curves were drawn for all the struts tested. From these the modulus of elasticity and the proportional elastic limit given in Table 3 were obtained.

There were eight struts of length 3 feet 1⅞ inches. The strut C–6 was cross-grained and broke suddenly at a load which was low for a strut from this plank. Strut A–4 had a curved grain near one of the pins, evidently due to a knot in the log near plank 4 at this point. This strut failed by shear along the curved grain. As these two results were evidently lower than the normal, two additional struts, B–$2_a$ and B–$2_b$, were cut from the long strut B–2 after it had been tested to its maximum load; and a third strut, C–3, was taken from the 10 foot 6¼ inch strut, C–3. The results from these three struts were used with those from the original five struts in calculating the average ultimate strength for this length.

## 2. TEST OF FORMULAS

Curve *I* of Fig. 4 is plotted with slenderness ratios as abscissas and the average ultimate strengths of each length as ordinates. The figure also shows the maximum and minimum ultimate strengths of each set. From Table 3 it is seen that all the struts from plank 1, except A–1, gave a low modulus of elasticity and a low ultimate strength. For the slenderness ratio of 150, for instance, E–1 has an ultimate strength of only 1200 pounds per square inch, while the next one has 1993 pounds per square inch. If the results from plank 1 were omitted from Fig. 4, the range from minimum to maximum would be greatly reduced.

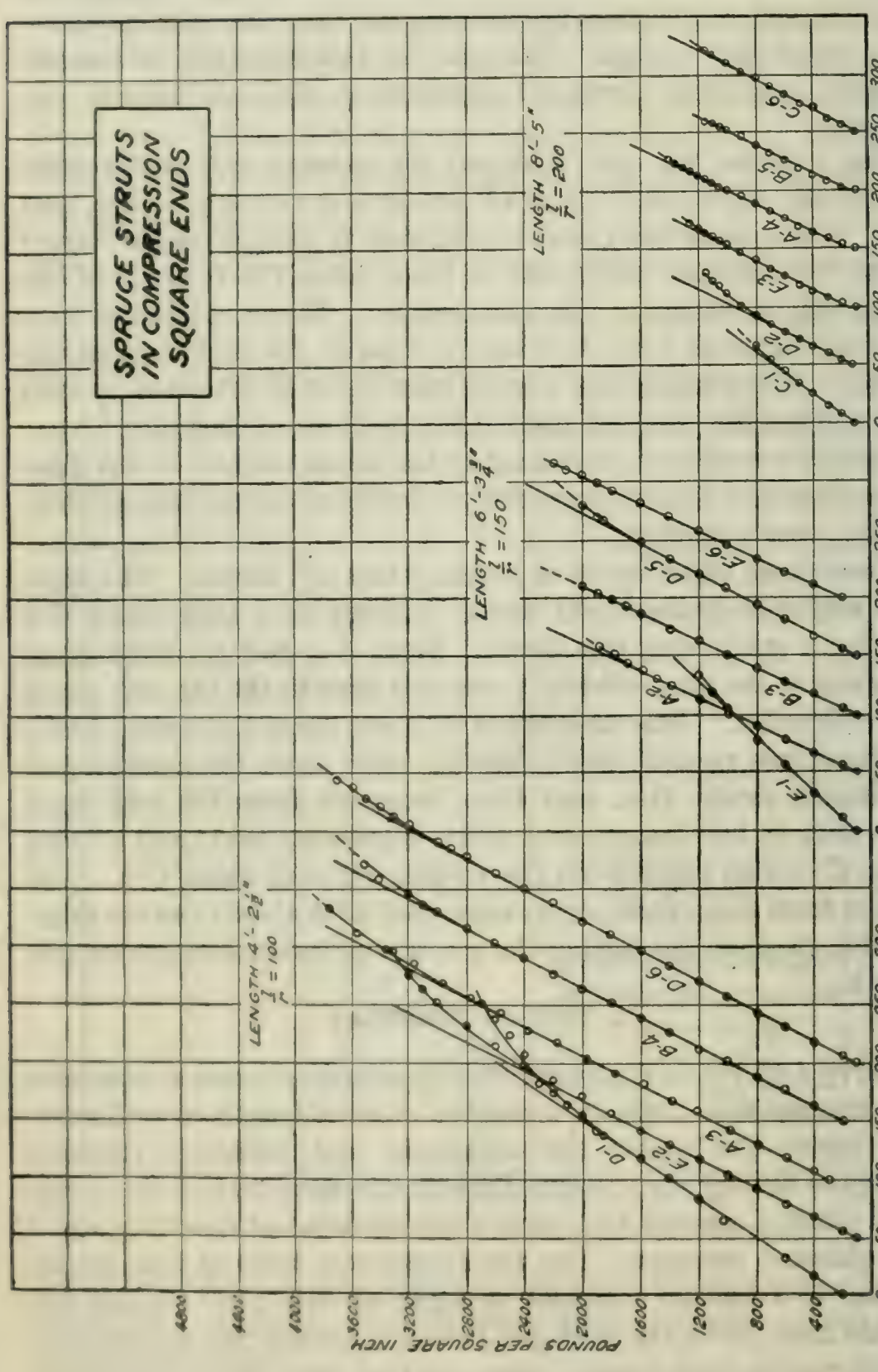


FIG. 3.—*Compression curves of three groups of square-end spruce struts*

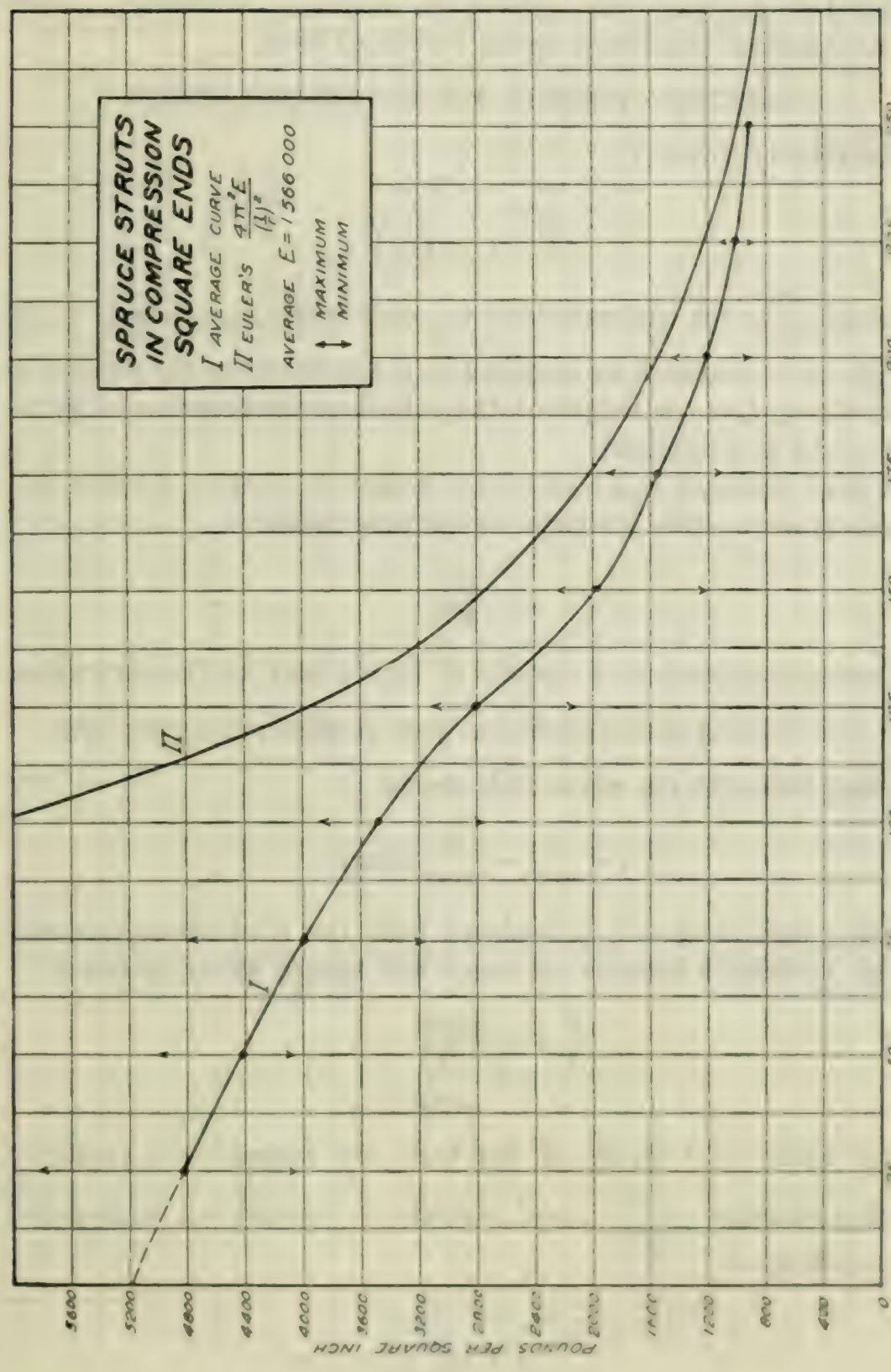


FIG. 4.—*Relation of ultimate strength of square-end* **spruce struts** *to slenderness ratio, and comparison with Euler's curve*

The average E from all these square-end struts is 1 566 000 pounds per square inch. Curve *II* of Fig. 4 is plotted from Euler's formula, with this value of the modulus of elasticity, under the assumption that these struts had fixed ends.

### 3. RANKINE'S FORMULA FOR SQUARE-END STRUTS

Rankine's formula is

$$\frac{P}{A}=\frac{S_u}{1+q\left(\frac{L}{r}\right)^2}$$

in which $\frac{P}{A}$ is the ultimate load in pounds per square inch, $S_u$ is the ultimate compressive strength of the material in the form of a short block, $L$ is the length of the column, $r$ is its radius of gyration, and $q$ is a constant.

Ritter's rational value of $q$, which makes Rankine's curve approach Euler's curve for large slenderness ratios, is

$$q=\frac{S_u}{\pi^2 E}.$$

From the extension of curve *I* of Fig. 4 back to the zero value of $\frac{L}{r}$, it is evident that $S_u$ is about 5200 pounds per square inch.

Using this with the value of $E$ above,

$$q=\frac{1}{2970}=\frac{1}{3000} \text{ nearly.}$$

Using this value of $q$ (calculated from the $E$ of the square-end tests), Rankine's formula for round-end spruce struts becomes

$$\frac{P}{A}=\frac{5200}{1+\frac{L^2}{3000\,r^2}}$$

For square-end struts, if the ends are regarded as perfectly fixed, $q$ becomes $\frac{1}{12\,000}$ and Rankine's formula for square-end spruce struts is

$$\frac{P}{A}=\frac{5200}{1+\frac{L^2}{12\,000\,r^2}}.$$

Fig. 5 shows Rankine's curve plotted from this last formula, the small circles of the figure being the average results of the test (used in plotting curve *I* of Fig. 4). It is evident that the formula

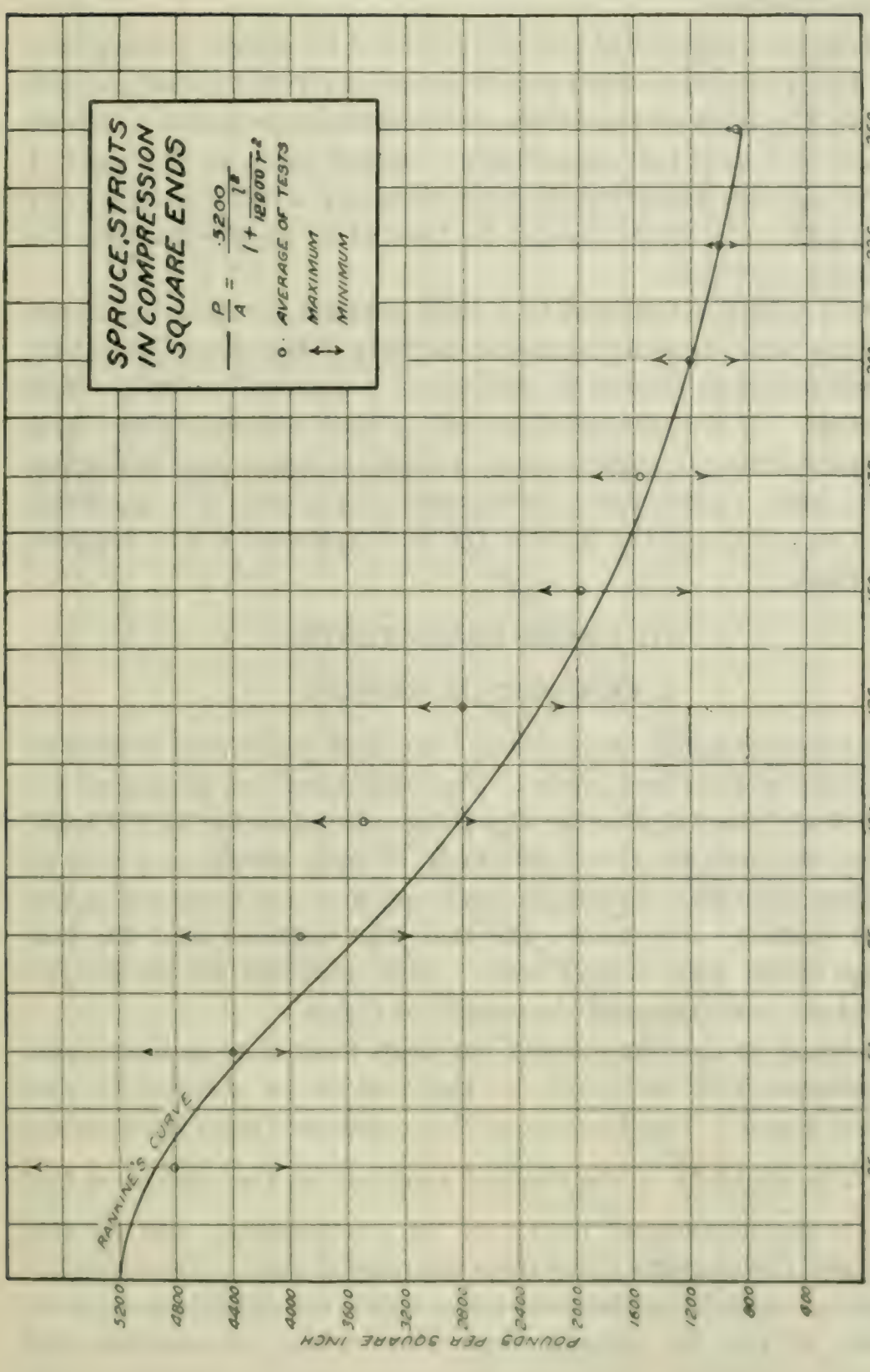


FIG. 5.—*Experimental results for square-end struts compared with Rankine's curve*

gives a fair approximation to the experiments except for the slenderness ratios from 75 to 150, within which range the error is on the side of safety.

It must be remembered that the heads of the Emery testing machine were practically fixed planes for these struts of small section and that the ends of the struts were carefully prepared. Where the ends of a strut rest on a flexible support, such as the spars of an airplane, this condition of approximately fixed ends does not obtain, and such struts should be treated as approximating the round-end condition.

A strut which is fastened to a rigid support by means of a pin frequently behaves as a round-end member in the plane of the pin. This was found to be true in the case of a stream-line strut which was tested. If it is desired that such a strut should behave as a fixed-end member, a stiffer connection and a longer and stiffer pin must be used. Also, since the moment at the ends of a fixed-end strut is as great as at the middle, the section should not be reduced at the ends.

## IV. CROSS-BEND TESTS

### 1. EXPERIMENTAL RESULTS

One cross-bend test piece taken from each plank was loaded at the middle of a 24-inch span. The deflection was measured by means of an Ames dial under the point of application of the load. The dial was held by two rods which, in turn, rested on a pair of transverse pins placed through the beam over the supports at the neutral surface. For safety the dial was removed and the last readings taken with a steel scale. This accounts for the irregularity of the last points of the curves of Fig. 6.

The stress in the outer fibers has been plotted as ordinate and the corresponding deflection at the middle as abscissa in the curves of Fig. 6. The fiber stress, $S$, is calculated from the formula $S = \frac{Mc}{I}$, in which $M$ is the bending moment at the middle of the span, $I$ is the moment of inertia of the cross-section, and $c$ is the distance of the extreme fibers from the neutral axis. The straight-line part of each curve has been extended to the deflection 0.2 inch in order to get the average slope from which to compute the modulus of elasticity ($E$). The deflection $y$ at the middle of the span, is given by

$$y = \frac{PL^3}{48\ EI}$$

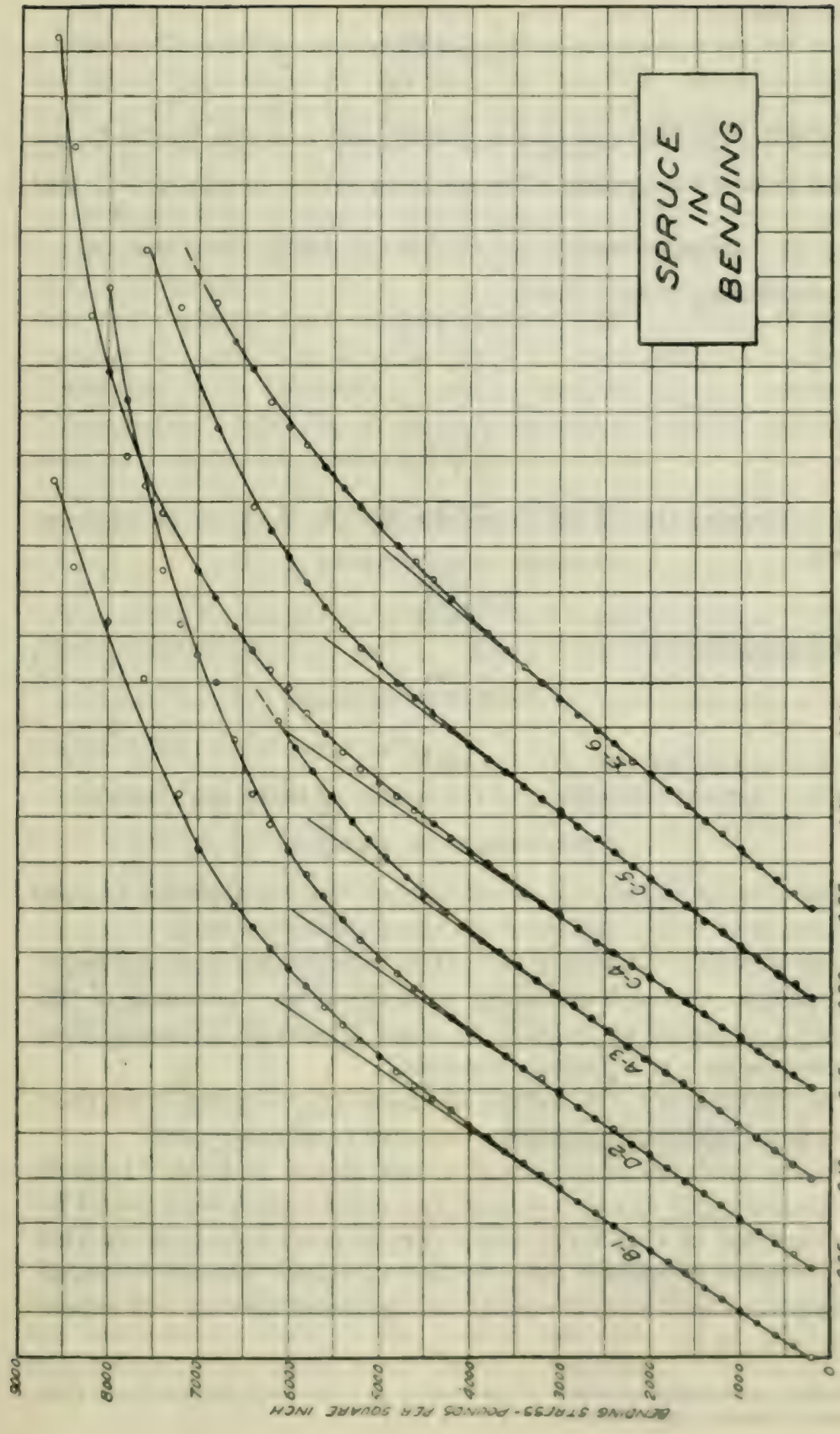


FIG. 6.—*Deflection at middle and maximum computed unit stress for spruce beams loaded at middle*

from which

$$E = \frac{PL^3}{48\ Iy}$$

in which $P$ is the load at the middle and $L$ is the length of the beam between supports. The moment at the middle is $\frac{PL}{4}$, and $c$ for a rectangular section is $\frac{d}{2}$, if $d$ is the depth of the section.

Substituting these values,

$$S = \frac{PL\ d}{8\ I},$$

or

$$\frac{PL}{8\ I} = \frac{S}{d}.$$

Substituting this in the expression for the modulus of elasticity gives

$$E = \frac{SL^2}{6y\ d}.$$

This reduces to

$$E = \frac{480\ S}{d},$$

for $L = 24$ inches and $y = 0.2$ inch.

Table 4 gives a summary of the results of these calculations.

### 2. DISCUSSION OF RESULTS

The average modulus of elasticity from the six tests is 1 513 000 as compared with 1 566 000 from the compression tests.

The moduli of rupture given in this table are considerably below the average values found from tests of spruce specimens of this size. A modulus of rupture of from 10 000 to 12 000 pounds per square inch is frequently obtained.[1]

On the contrary, the moduli of elasticity computed from these data agree with average values obtained from other tests.

As the modulus of rupture does not appear in Euler's formula for the strength of columns, and the usual values were found for the modulus of elasticity, which does appear, it is believed that the formula developed here applies to spruce having a greater strength, as well as to the particular material used in this experimental work.

[1] Bulletin 126—Mechanical Properties of Woods Grown in the United States, published by the Forest Products Laboratory, Madison, Wis.

Test piece E–6 was cross-grained and failed diagonally. Its modulus of elasticity was lower than that obtained from the other specimens from plank 6. On the other hand, B–1 gave a higher modulus of elasticity than most of the struts from plank 1. The difference between the values of the modulus of elasticity by the two methods is not large. Where it is not convenient to make compression tests of long struts, the modulus of elasticity may be determined from cross-bend tests; and this modulus may be used in Euler's formula.

If short blocks are tested in compression, the ultimate compressive strength thus obtained may be used with the modulus of elasticity from the bending tests to compute Ritter's constant. This constant, with the ultimate compressive strength, makes it possible to write a formula of the Rankine type.

## V. ROUND-END STRUTS

### 1. EXPERIMENTAL RESULTS

The struts for the round-end tests were taken from three 16-foot planks numbered 7, 8, and 9. There were eight lengths from $\frac{L}{r}=25$ to $\frac{L}{r}=200$. The ends were finished in the same way as the struts for the square-end tests.

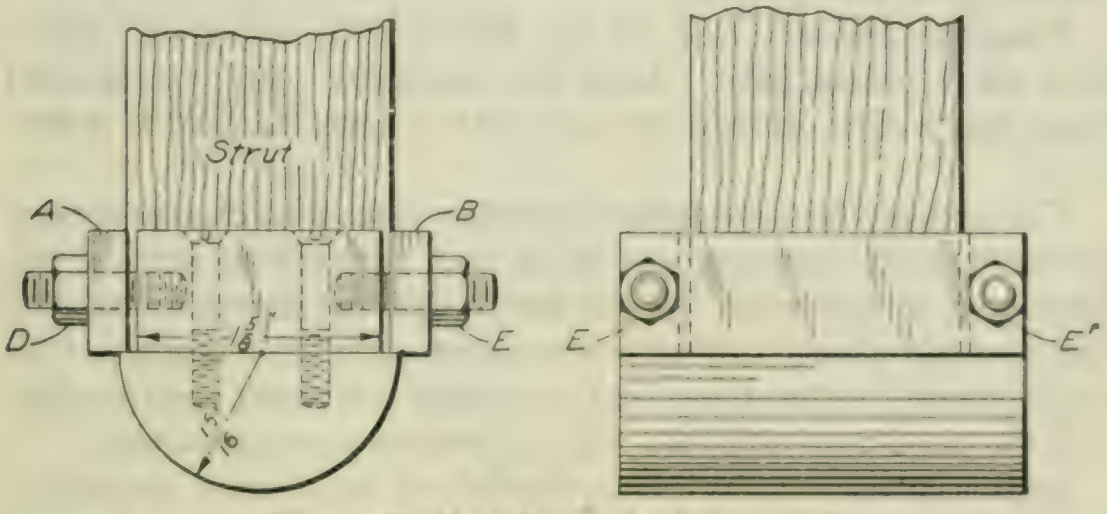


FIG. 7.—*Steel heads for round-end spruce struts*

To secure the round-end condition, the head shown in Fig. 7 was attached to each end. The ends of the struts were secured to steel half cylinders (diameter = 1 7/8 inches), which rested against the compression heads of the testing machine. They therefore rolled with little friction when the strut deflected.

The cylinders were attached to the struts by means of the plates *A* and *B* held by the nuts *D*, *D'*, *E*, and *E'*. The strut was placed in the machine with the axes of the cylinders horizontal. If the strut showed considerable deflection in the vertical plane when a load of several hundred pounds was applied, the pressure was released to about 300 pounds and the position of the cylindrical bearing blocks shifted by turning the nuts. It was possible in this way to change the line of application of the loads as much as one-sixteenth of an inch on either side of the center. This insured axial loading and compensated for any lack of straightness in the strut.

Table 5 gives the results for one round-end strut. It will be noticed that the vertical deflection was small up to one-half the maximum load, and the horizontal deflection almost negligible until a comparatively large load was reached. At the total load of 3050 pounds the vertical deflection was 0.312 inch. Without compressing the strut further the deflection continued to increase and the load decreased. The load was again brought to 3050 pounds, and the deflection was found to be 0.482 inch. After the Howard gages and counterweights had been removed, the load was 2980 pounds. Further compression developed a maximum load of 3025 pounds, which under continued compression decreased to 3015 pounds.

This was characteristic of the behavior of round-end struts with small eccentricity. After the maximum load was reached there was a slow decrease of load, with a large increase of deflection.

The zero of the large Emery machine shifts with change of temperature, and, therefore, the beam was adjusted to zero at the beginning of each test. At the end of this test it was found that the zero had changed by an amount equivalent to a negative load of 30 pounds, so that the actual maximum was about 3020 pounds, and the maximum unit load was 990 pounds per square inch.

As this correction was known for the last values only, the stress-strain diagrams have been plotted from the loads as read, but the corrected values of the ultimate unit loads have been used in drawing the curves of ultimate strength and slenderness ratios. These corrections were not made in the case of the square-end struts.

## 2. TESTS OF FORMULAS

Fig. 8 shows the stress-strain diagrams and the horizontal and vertical deflections for the strut of Table 5. Diagrams were

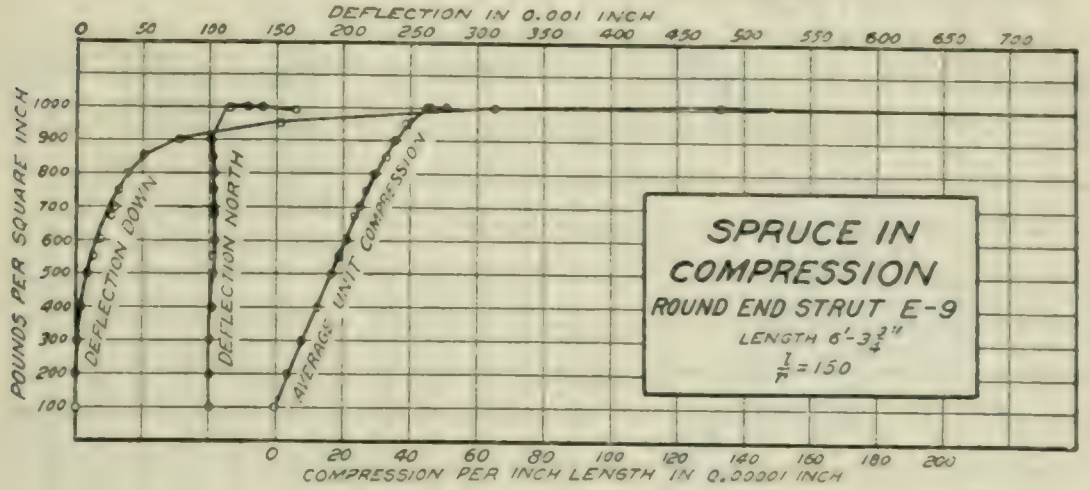
DEFLECTION IN 0.001 INCH
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700
POUNDS PER SQUARE INCH
1000 900 800 700 600 500 400 300 200 100
DEFLECTION DOWN
DEFLECTION NORTH
AVERAGE UNIT COMPRESSION
SPRUCE IN COMPRESSION
ROUND END STRUT E-9
LENGTH 6'-3 3/4"
l/r = 150
0 20 40 60 80 100 120 140 160 180 200
COMPRESSION PER INCH LENGTH IN 0.00001 INCH

FIG. 8.—*Deflection and compression of round-end spruce strut*

plotted for each round-end strut similar to those of the square-end struts shown in Fig. 3. From these the modulus of elasticity and the proportional limit were determined for each strut. A summary is given in Table 6.

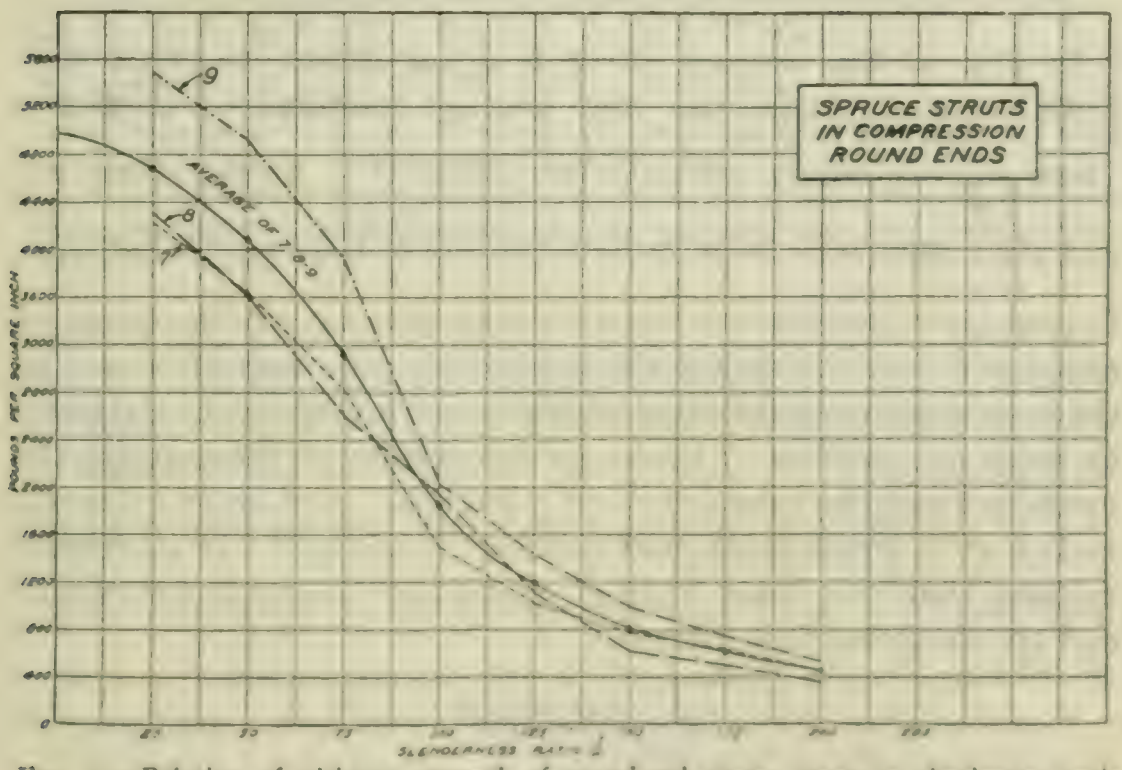


FIG. 9.—*Relation of ultimate strength of round-end spruce struts to slenderness ratio*

The curve of slenderness ratio and ultimate load for the struts from each plank, together with the average curve, is shown in Fig. 9. The average modulus of elasticity from all the tests is

1 910 000 pounds per square inch, which is large for spruce, and is due to the exceptionally large values of the modulus for all the struts from plank 9.

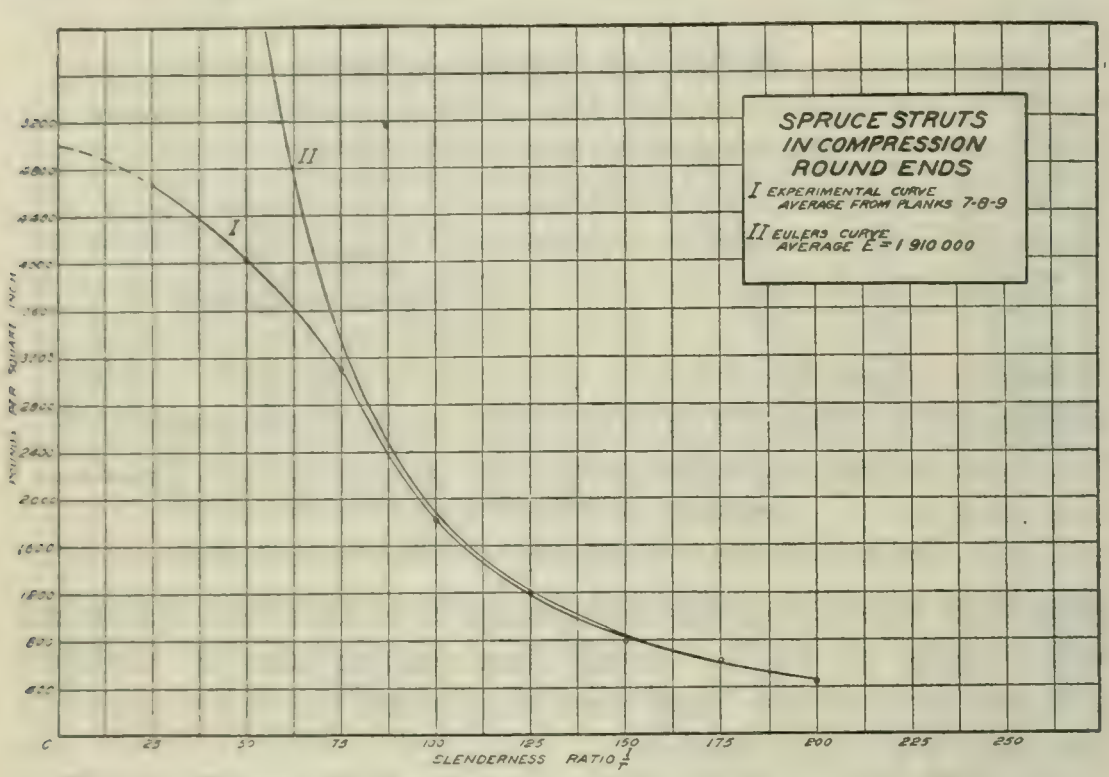


FIG. 10.—*Experimental curve for round-end spruce struts compared with Euler's*

In Fig. 10 the average curve is again shown, together with Euler's curve plotted for the average modulus of elasticity. These curves nearly coincide for values of $\frac{L}{r}$ greater than 100 and their difference is small for values of $\frac{L}{r}$ between 80 and 100. It is evident that Euler's formula may be used in the design of round-end timber struts if the slenderness ratio exceeds 100. In the case of spruce it is not advisable to use a modulus of elasticity as great as 1 900 000. Based on the results of these tests, the modulus should be taken as about 1 600 000. A value of 1 622 000 makes $\pi^2 E$ equal the round number 16 000 000. It is recommended that this value be used, and Euler's formula for round-end spruce struts then becomes

$$\frac{P}{A} = \frac{16\,000\,000}{\left(\frac{L}{r}\right)^2}.$$

This formula should be used for values of the slenderness ratio greater than 100, and may be used, with small error, for values between 80 and 100.

Fig. 11 gives the theoretical curve for round-end struts with slightly eccentric loads. It is plotted from the formula

$$S_u = \frac{P}{A}\left[1 + \frac{ec}{r^2} \cdot \sec\left(\sqrt{\frac{P}{AE}} \cdot \frac{L}{2r}\right)\right]$$

where $S_u$ is the ultimate compressive strength of a short block, $\frac{P}{A}$ is the ultimate unit load on a given strut, $c$ is the distance from the

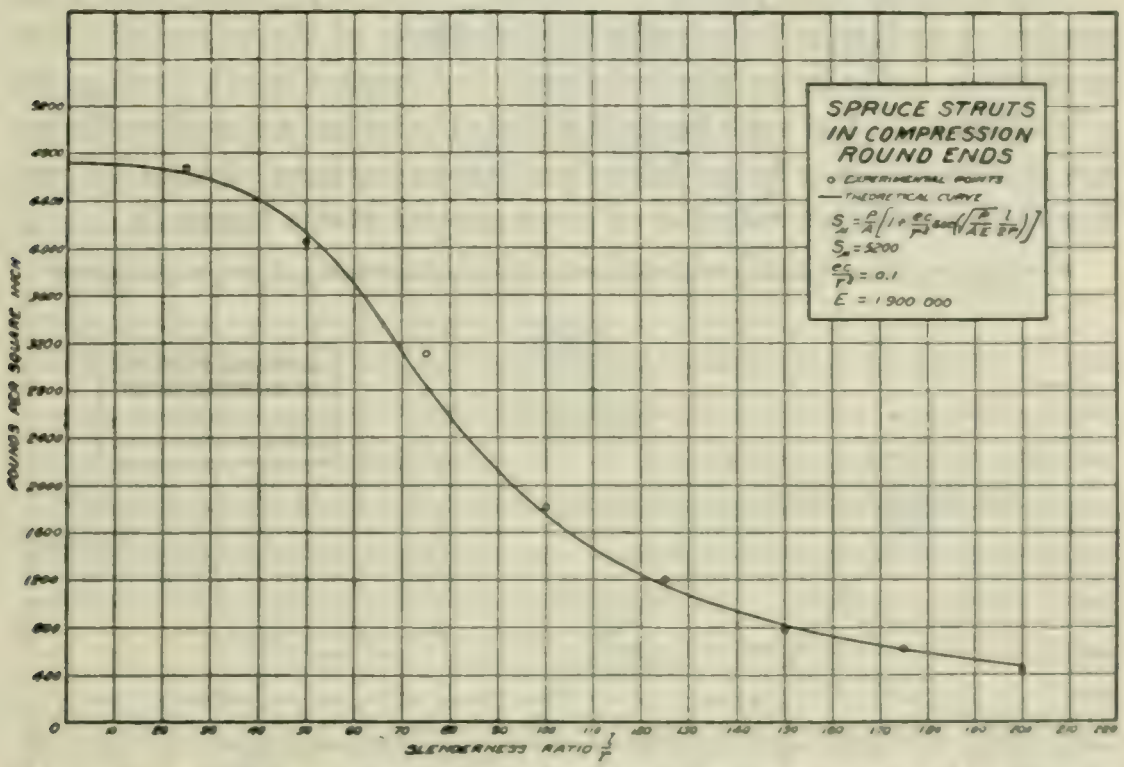


FIG. 11.—*Experimental results for round-end spruce struts compared with theoretical curve for a perfectly straight and uniform strut with round ends and slightly eccentric load*

center of gravity of the section to the extreme fiber, $e$ is the eccentricity of the load, $r$ is the radius of gyration, $E$ is the modulus of elasticity, and $L$ is the length of the strut. In calculating the data for this curve, $S_u$ was taken as 5200 pounds per square inch, $E$ as 1 910 000 pounds per square inch, and $\frac{ec}{r^2}$ assumed to be 0.1, which corresponds to an average eccentricity of $\frac{7}{240}$ inch for a section 1.75 inches square, free to turn about an axis parallel to one face, but not to turn about a diagonal of the section.

The small circles in Fig. 11 represent the the average experimental values of Table 6, from which curve *I* of Fig. 10 was drawn. From the close agreement of these points with the theoretical curve it is evident that it is only necessary to determine the ultimate strength of short blocks in compression and the modulus of

elasticity of the material in order to construct working curves for struts of all lengths. The modulus of elasticity may be determined from bending tests.

The amount of eccentricity is an uncertain element, and although a considerable difference in eccentricity makes little difference in the strength of long struts, it is always a questionable factor in the strength of short struts, no matter what formula is used.

The tests of long pieces by bending or compression should be carried to failure to determine the brashness of the material. The maximum loads in an airplane strut are impact loads (lasting for a brief time). For such loads, a wood of large modulus of resilience (as evidenced by a large deflection before rupture) should be preferred to a brasher material of even greater static strength.

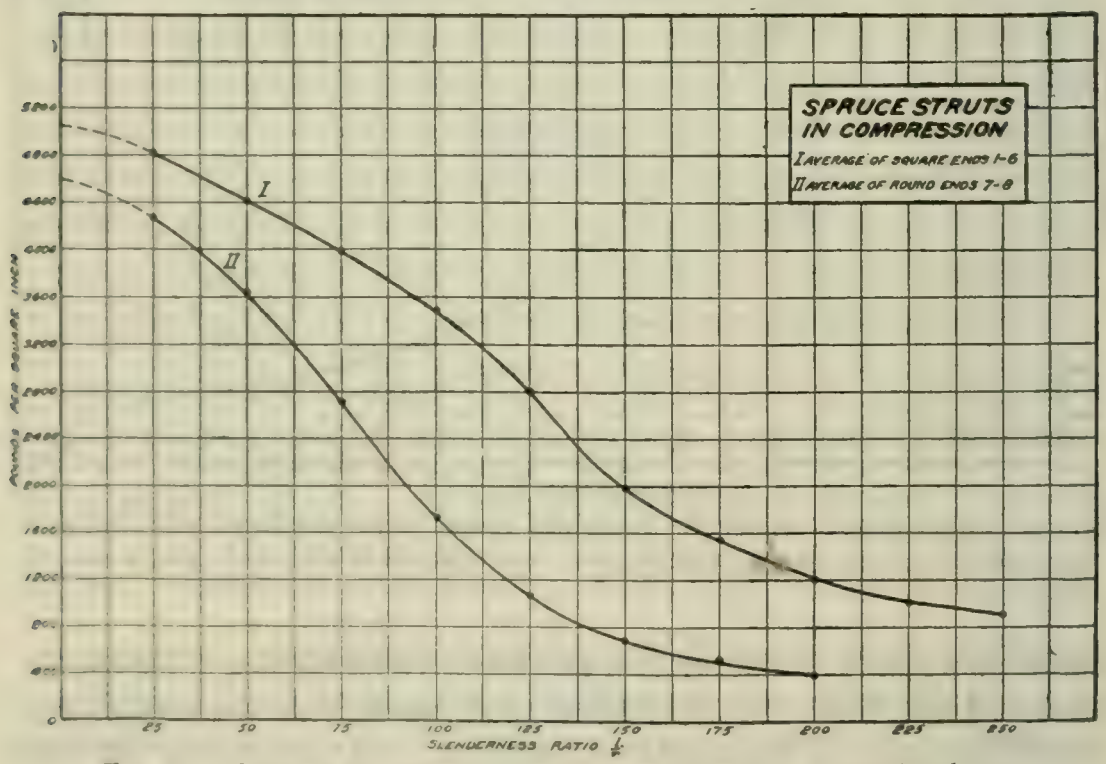


FIG. 12.—*Comparative ultimate strength of square-end and round-end struts*

Fig. 12 gives a comparison of round-end and square-end struts. Curve *I* is the mean of all the square-end struts, for which the average modulus of elasticity is 1 566 000 pounds per square inch. Curve *II* is the mean of the round-end struts from planks 7 and 8, for which the average modulus of elasticity is 1 670 000 pounds per square inch. The results from plank 9 are not included, as its large modulus increases the average of the round-end struts so as to vitiate the comparison.

## VI. CONCLUSIONS

Euler's formula gives accurate results in the design of round-end spruce struts for values of $\frac{L}{r}$ greater than 100 and may be used with little error for values between 80 and 100.

For the ultimate strength per square inch for round-end spruce struts it is recommended that Euler's formula be written

$$\frac{P}{A} = \frac{16\,000\,000}{\left(\frac{L}{r}\right)^2}$$

which corresponds to a modulus of elasticity of 1 622 000 pounds per square inch.

For short round-end spruce struts use the Rankine formula

$$\frac{P}{A} = \frac{5200}{1 + \frac{L^2}{3000r^2}}.$$

For square-end struts fitted accurately to rigid bodies, use the Rankine formula

$$\frac{P}{A} = \frac{5200}{1 + \frac{L^2}{12000r^2}}.$$

If the ends are not well fixed, use values of the constant between

$$\frac{1}{12\,000} \text{ and } \frac{1}{3000}.$$

These formulas give the ultimate unit loads in pounds per square inch and must be divided by suitable factors of safety.

In the study of new materials a bending test may be made to determine the modulus of elasticity and the resilience, and a compression test of a short block to determine the ultimate compressive strength. The results thus obtained may be used in Euler's formula for round-end struts of uniform section having a slenderness ratio greater than 100 and in Rankine's formula for struts of all lengths. Instead of Rankine's formula, the theoretical equation of a strut with slightly eccentric load may be employed. This equation is more accurate than Rankine's formula, but the labor of computation is greater.

If long struts, having a slenderness ratio of 200 or more, be provided with round ends similar to Fig. 7, the modulus of elasticity may be determined quickly and accurately by means of

Euler's formula. Where a long compression machine is not available, a small strut may be tested by placing the lower end on a platform scale and applying pressure to the top by means of a lever until the buckling load is reached.

All timber for use in airplanes might be tested in this way as a part of the inspection. The pieces could be tested in the form of long strips before they are cut into short lengths. Where long strips are not available, a small test piece, not over 0.25 inch in thickness and of any convenient width, may be taken from each plank and tested to detruction as a round-end strut.

In all cases of square-end struts the amount of eccentricity is an uncertain factor, and the ends may seldom be regarded as fixed.

Ordinary airplane-pin connections should be regarded as round ends in the plane of the pins as well as in the plane perpendicular thereto.

## VII. THEORY OF CERTAIN TAPERED STRUTS[2]

### 1. SHAPE OF STRUT

The results of the preceding experiments show that the load, under which a slender wood strut of uniform cross section fails, is determined primarily by the modulus of elasticity of the material. The following discussion develops the theory of the failure of a certain kind of tapered strut by elastic bending.

In one form of tapered strut the moment of inertia of any section between one end and the middle is proportional to the square of its distance from a fixed point beyond that end of the strut. Also, both halves of the strut are symmetrical with respect to a transverse plane at the middle. This form approximates many of the types used in practice. In Fig. 13, $M$ is a point at a distance $a$ to the left of the left end of the strut. The moment of inertia of any section in the left half, at a distance $x$ from $M$, is given by

$$I = Cx^2,$$

where $C$ is a constant depending upon the form of the strut. Likewise $N$ is a point at a distance $a$ to the right of the right end of the strut. The moment of inertia of any section in the right half is expressed by the same relation, with $x$ measured to the left from $N$.

[2] A number of papers have been published in recent years on tapered struts. Arthur Morley (Engineering, **97**, pp. 566–568, and **104**, pp. 295–298), L. Bairstow and E. W. Stedman (Engineering, **98**, pp. 492–494), and John Case (Engineering **106**, pp. 295–298) have given methods of successive approximation, either graphic or analytic, for struts of arbitrarily varying cross section. W. M. Wallace (Engineering, **91**, pp. 831–832) has discussed by approximate methods columns whose moment of inertia varies according to an assumed analytical law. Since the present paper was in print, Akimasa Ono (Memoirs of the College of Engineering, Kyusha Imperial University, Fukuoka, Japan, **1**, No. 5, pp. 395–406) has given exact solutions for columns resembling those here discussed. In the latter two cases, however, the cross sections of the columns vanish at the end, whereas the columns here discussed have a finite cross section at the end.

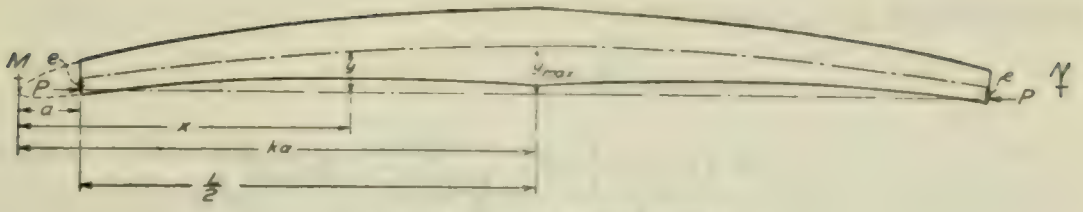


FIG. 13.—*Bent tapered strut*

## 2. DERIVATION OF FORMULAS

The load on this strut is $P$ pounds acting at a distance $e$ from the center of gravity of the end sections. Let $y$ be the distance of the center of gravity of any section of the bent strut from the line of action of the load. The differential equation of the elastic curve for this strut is

$$EI\frac{d^2y}{dx^2} = -Py.$$

Substituting $I = Cx^2$, transposing and dividing by $EC$,

$$x^2\frac{d^2y}{dx^2} + \frac{Py}{EC} = 0.$$

This is a homogeneous linear differential equation of the second order. Its solution is written in three standard forms depending on the value of $\frac{4P}{EC}$.

$$\text{If } \frac{4P}{EC} < 1, \quad y = A_1\left(\frac{x}{a}\right)^{+\frac{1}{2}\sqrt{1-\frac{4P}{EC}}} + B_1\left(\frac{x}{a}\right)^{\frac{1}{2}-\frac{1}{2}\sqrt{1-\frac{4P}{EC}}}$$

$$\text{If } \frac{4P}{EC} = 1, \quad y = \left(\frac{x}{a}\right)^{\frac{1}{2}}\left\{A_2 + B_2 \log\left(\frac{x}{a}\right)^{\frac{1}{2}}\right\}$$

$$\text{If } \frac{4P}{EC} > 1, \quad y = A\left(\frac{x}{a}\right)^{\frac{1}{2}} \sin\left\{B + \sqrt{\frac{4P}{EC} - 1}\,\log\left(\frac{x}{a}\right)^{\frac{1}{2}}\right\} \qquad (1)$$

These solutions may be verified by differentiating and substituting in the original equation. $A_1$, $B_1$, $A_2$, $B_2$, and $A$ are integration constants having the dimensions of a length, and $B$ is a dimensionless integration constant.

The constant $C$ is generally a small quantity and for loads which cause failure the fraction $\frac{4P}{EC}$ is greater than unity, so that only the third form of the solution need be used. To determine the constants in equation (1) we have the boundary conditions: At the end of the strut $x = a$, $y = e$, at the middle of the strut $x = ka$, $y = y_{max.}$, $\frac{dy}{dx} = 0$, $k = 1 + \frac{L}{2a}$.

Substituting in equation (1)

$$e = A \sin B$$

$$y_{max} = Ak^{\frac{1}{2}} \sin\left( B + \sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}} \right)$$

$$= Ak^{\frac{1}{2}} \sin \alpha \qquad (2)$$

Differentiating equation (1)

$$\frac{dy}{dx} = \frac{1}{2a} A \left(\frac{x}{a}\right)^{-\frac{1}{2}} \sin\left(B + \sqrt{\frac{4P}{EC} - 1} \log \left(\frac{x}{a}\right)^{\frac{1}{2}}\right)$$

$$+ \sqrt{\frac{4P}{EC} - 1} \cos\left(B + \sqrt{\frac{4P}{EC} - 1} \log \left(\frac{x}{a}\right)^{\frac{1}{2}}\right)$$

Substituting $x = ka$ and equating to zero

$$\frac{1}{2a} Ak^{-\frac{1}{2}} \left[ \sin \alpha + \sqrt{\frac{4P}{EC} - 1} \cos \alpha \right] = 0$$

or

$$\tan \alpha = -\sqrt{\frac{4P}{EC} - 1}$$

Then

$$B = \alpha - \sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}}$$

and

$$A = \frac{e}{\sin B}$$

Substituting in equation (2)

$$y_{max} = \frac{ek^{\frac{1}{2}} \sin \alpha}{\sin B}$$

$$= \frac{ek^{\frac{1}{2}} \sin \alpha}{\sin \alpha \cos\left(\sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}}\right) - \cos \alpha \sin\left(\sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}}\right)}$$

or

$$y_{max} = \frac{ek^{\frac{1}{2}}}{\cos\left(\sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}}\right) + \frac{1}{\sqrt{\frac{4P}{EC} - 1}} \sin\left(\sqrt{\frac{4P}{EC} - 1} \log k^{\frac{1}{2}}\right)} \qquad (3)$$

### 3. APPLICATION OF FORMULAS

This equation may be used to calculate the maximum fiber stress in the strut under any known eccentric load.

Use the formula,

$$S = \frac{P}{A} + \frac{Mc}{I}$$

where $A$ is the area of the section, $M$ is the bending moment at the section, and $c$ is the distance of the extreme fibers from the center of gravity of the section. In the equations of a strut $M = Py$ if $y$ is measured from the line of the load, as in Fig. 13. At the ends of the strut $M = Pe$, at the middle $M = Py_{max}$, at the other sections $M = Py$ where $y_{max}$ and $y$ may be calculated from equations (3) and (2), respectively. Generally it is only necessary to calculate the stress at the middle and at the ends of the strut. In a strut for which $I = Cx^2$ the maximum stress occurs a short distance from the middle. The difference between the maximum stress and the stress at the middle section is not great.

The maximum safe load—that is, the load which gives the maximum safe fiber stress—can thus be determined by a process of trial and error.

For relatively slender struts a simpler method may be used. If the load is assumed to be centrally applied ($e = o$) and $P$ so chosen as to make the denominator in equation (3),

$$\cos\left(\sqrt{\frac{4P}{EC} - 1}\ \log k^{\frac{1}{2}}\right) + \frac{1}{\sqrt{\frac{4P}{EC} - 1}} \sin\left(\sqrt{\frac{4P}{EC} - 1}\ \log k^{\frac{1}{2}}\right) \quad (4)$$

equal to zero, or in another form to make

$$\tan \alpha \log k^{\frac{1}{2}} = -\alpha \quad (5)$$

the deflection $y$ become indeterminate as in a strut of uniform cross section under Euler's load. Equation (5) is, in fact, a generalization of Euler's formula for this type of tapered strut and, as will be shown later, reduces to Euler's formula when $k = 1$.

In practice the eccentricity is seldom known, but in slender struts to which these equations are applicable the effect of eccentricity is small and the ultimate load in practice is only slightly less than that given by equation (5).

From inspection of the equation it is evident that the critical load is that which makes the angle $\left(\sqrt{\frac{4P}{EC} - 1}\ \log k^{\frac{1}{2}}\right) = -\tan \alpha$ $\log k^{\frac{1}{2}}$ a little greater than $\frac{\pi}{2}$. The cosine will then be negative and the sine positive.

To determine whether a given load is safe, multiply the load by a suitable factor of safety and substitute in expression (4). If the angle $\left(\sqrt{\frac{4P}{EC}} - 1 \log k^{\frac{1}{2}}\right)$ is less than $\frac{\pi}{2}$ radians, the load is a safe one. If the angle is greater than $\frac{\pi}{2}$ radians, the load is still safe provided expression (4) is positive. If it is negative, the load is too large.

Before applying these equations it is necessary to express $C$ and $k$ in terms of the dimensions of the strut. Let $I_1$ be the moment of inertia at the end (where $x = a$), and let $I_2$ be the moment of inertia at the middle (where $x = ka$).

$$I_1 = C\ a^2; \quad I_2 = C(ka)^2;$$

$$k^2 = \frac{I_2}{I_1}.$$

Since

$$ka = a + \frac{L}{2},$$

$$\sqrt{I_1} = \sqrt{C}\ a; \quad \sqrt{I_2} = \sqrt{C}\left(a + \frac{L}{2}\right);$$

$$\sqrt{C} = \frac{\sqrt{I_2} - \sqrt{I_1}}{\frac{L}{2}}.$$

If all sections of the strut are similar figures, so that $I$ varies as the fourth power of the transverse dimensions,

$$k = \frac{D_2^2}{D_1^2}; \quad k^{\frac{1}{2}} = \frac{D_2}{D_1},$$

where $D_2$ and $D_1$ are homologous transverse dimensions at the middle and ends of the strut, respectively.

The maximum load which a given strut will carry may be found by the method of trial and error. This method of applying the formula is shown in the example which follows. The expression (4) is used instead of equation (5) because the interpolation is more nearly linear.

EXAMPLE.—A wooden strut is 6 feet long, 2 inches square at the middle, 1.6 inches square at the ends, and tapers according to the law $I = Cx^2$. If the modulus of elasticity $(E) = 1\ 600\ 000$ pounds per square inch, find the ultimate load.

$$k^{\frac{1}{2}} = \frac{D_2}{D_1} = \frac{2}{1.6} = \frac{5}{4}$$

$$\log_e k^2 = 1.60944 - 1.38629 = 0.22315$$

$$I_1 = \frac{1.6^4}{12}; \quad I_2 = \frac{2^4}{12}; \quad \sqrt{C} = \frac{2^2 - 1.6^2}{\sqrt{12 \times 36}}; \quad C = \frac{(4 - 2.56)^2}{12 \times 36^2} = \frac{1}{7500}$$

By Euler's formula the ultimate strength of a uniform strut 2 inches square and 72 inches long is

$$P = \frac{\pi^2 \times 1\,600\,000 \times 16}{72 \times 72 \times 12} = 4061.5 \text{ pounds.}$$

The load on the tapered strut must be considerably smaller. First try 3000 pounds.

$$\frac{4P}{EC} = \frac{3000 \times 4 \times 7500}{1\,600\,000} = 56.25$$

$$\sqrt{\frac{4P}{EC} - 1} = \sqrt{55.25} = 7.433$$

$$7.433 \times 0.22315 = 1.6605 \text{ radians} = 95^\circ\ 8'$$

$$\text{Cos } 95^\circ\ 8' + \frac{\sin 95^\circ\ 8'}{7.433} = -0.0895 + 0.1338 = 0.0443$$

The load of 3000 pounds is below the ultimate.

Next try 3200 pounds.

$$\sqrt{\frac{4P}{EC} - 1} = \sqrt{59} = 7.6811$$

$$\frac{7.6811 \times 0.22315 \times 180}{\pi} = 98.205^\circ = 98^\circ\ 12'$$

$$\text{Cos } 98^\circ\ 12' + \frac{\sin 98^\circ\ 12'}{7.6811} = -0.1426 + 0.1289 = -0.0137$$

This load is too great. Interpolating

$$P = 3000 + \frac{443 \times 200}{443 + 137} = 3153$$

Recalculating with $P = 3153$ pounds,

$$\sqrt{\frac{4P}{EC} - 1} = 7.6236; \quad \theta = 97^\circ\ 28'$$

$$\text{Cos } 97^\circ\ 28' + \frac{\sin 97^\circ\ 28'}{7.6236} = -0.1299 + 0.1301 = 0.0002$$

Interpolating again,

$$P = 3153 + \frac{2 \times 47}{139} = 3153.7 \text{ pounds}$$

The ratio of this load to Euler's ultimate load on a uniform strut 2 inches square is $\frac{3153.7}{4061.5}=0.7765$. We will call this the strength ratio of the strut. It will be shown later that this ratio holds for a strut of any length and material for which $k^2=1.25$, provided the slenderness ratio is such that Euler's formula is applicable for the strut of uniform section.

While it is not practicable to solve equation (5) for $P$ when $k$ is given, except by the method of trial and error, it is easy to find the value of $k$ corresponding to any given figure for $\frac{4P}{EC}$ and from a series of such values plot a curve which will simplify the computations.

Solving equation (5) for ($\kappa$), $\log_e k=\frac{2\alpha}{\tan\alpha}$ (6)

where $\tan\alpha=\sqrt{\frac{4P}{EC}-1}$ which determines $\frac{4P}{EC}$ as a function of $k$. The first part of Table 7 gives the calculation for $k$ by logarithms.

STRENGTH RATIO.—The ratio between the ultimate load of this type of tapered strut and Euler's ultimate load of a strut of uniform cross section whose length is the length of the tapered strut and whose moment of inertia is the maximum moment of inertia of the tapered strut, is independent of the length and moment of inertia and depends for its value on $k$ alone. This ratio will be called the strength ratio of the tapered strut. To calculate this ratio, it is necessary to express $C$ in terms of $I_2$, $L$, and $k$ and substitute in $\frac{4P}{EC}$, which is known from equation (6) or Table 7 as a function of $k$.

$$\sqrt{C}=\frac{\sqrt{I_2}-\sqrt{I_1}}{\frac{L}{2}}=\frac{\sqrt{I_2}-\frac{\sqrt{I_2}}{k}}{\frac{L}{2}}=2\frac{\sqrt{I_2}}{L}\left(1-\frac{1}{k}\right)$$

$$C=\frac{4I_2}{L^2}\left(1-\frac{1}{k}\right)^2$$

Substituting this value of $C$,

$$\frac{4P}{EC}=\frac{PL^2}{EI_2\left(1-\frac{1}{k}\right)^2}$$

from which,

$$\frac{PL^2}{EI_2}=\frac{4P}{EC}\left(1-\frac{1}{k}\right)^2 \qquad (7)$$

By Euler's formula the ultimate load of a strut of uniform section of length $L$ and moment of inertia $I_2$ is,

$$P' = \frac{\pi^2 E I_2}{L^2},$$

from which

$$\frac{P' L^2}{E I_2} = \pi^2. \tag{8}$$

Dividing (7) by (8), gives the strength ratio of the tapered strut

$$\frac{P}{P'} = \left(\frac{4P}{EC}\right) \cdot \frac{\left(1 - \frac{1}{k}\right)^2}{\pi^2}$$

which is seen to be a function of $k$ alone, as stated above.

The second part of Table 7 gives most of the steps of the calculations of the strength ratios for the values of $\frac{4P}{EC}$ in the first part of the table. It is to be noted that as $k$ approaches unity the strength ratio approaches unity showing that equation (5) reduces to Euler's formula for $k = 1$. The last column of the table gives $\sqrt{\frac{1}{k}}$.

$$\sqrt{\frac{1}{k}} = \left(\frac{I_1}{I_2}\right)^{\frac{1}{4}}$$

If all sections of the strut are similar figures,

$$\sqrt{\frac{1}{k}} = \frac{D_1}{D_2},$$

$D_1$ and $D_2$ being homologous transverse dimensions at the ends and middle of the strut, respectively.

The curve of Fig. 14 is plotted from Table 7, and gives the strength ratio for values of $\sqrt{\frac{1}{k}}$ above 0.2. Lower values are omitted as such struts will generally fail by compression at the ends. This curve affords an easy method of calculating the ultimate strength of a slender tapered strut for which the equation is $I = Cx^2$. Calculate the strength of a uniform strut of the same length and of cross section equal to the maximum section of the tapered strut and multiply this result by the strength ratio as read from the curve.

### 4. APPROXIMATE CALCULATIONS

The straight line of Fig. 14, at an angle of 45°, does not deviate greatly from the strength-ratio curve. For approximate calculations the strength ratio may be taken as equal to $\sqrt{\frac{I}{k}}$.

If all sections are similar figures, $\sqrt{\frac{I}{k}}=\frac{D_1}{D_2}$, and the strength of the tapered strut is to the strength of the uniform strut as a transverse dimension at the end is to the homologous transverse dimension at the middle.

Another approximate solution is by means of the moment of inertia at some point between the end and the middle. We will consider the section at one-third the length from the end; for the case, $\sqrt{\frac{I}{k}}=0.5$.

$$\frac{I}{k}=0.25;\quad k=4;\quad ka-a=3a=\frac{L}{2}.$$

$$x=a+\left(\frac{2}{3}3a\right)=3a.$$

$$I=Cx^2=9Ca^2.$$

$$I_2=C(ka)^2=16Ca^2.$$

$$\frac{I}{I_2}=\frac{9}{16}=0.5625.$$

The moment of inertia at one-third the length from the end is 56 per cent of that at the middle. If the moment of inertia at this section be taken as the average $I$ for use in Euler's formula, it will give an apparent strength ratio of 0.56. Fig. 14 shows that the real strength ratio is 0.49, an error of about 14 per cent in this case.

The second column of Table 8 gives the ratio of the moment of inertia at the third points to that at the middle for a series of values of $\sqrt{\frac{I}{k}}$. A comparison of these values, with the strength ratios in the last column, shows that the moment-of-inertia method may be used with little error for struts of moderate taper. Greater accuracy may be secured by taking, for any given value of moment-of-inertia ratio, the corresponding strength ratio from the last column of Table 8.

The third column of Table 8 gives the ratio of the moment of inertia at five-sixteenths of the length from the end, to the moment of inertia at the middle. These agree more closely with the strength ratios and err slightly on the side of safety in the case of struts of small taper.

These figures apply strictly to struts for which $I = Cx^2$. Actual struts taper less rapidly near the middle, so that the error in using the moment of inertia at the one-third point may be a little greater than indicated by Table 8.

## 5. RELATION OF THE STRENGTH OF A STRUT TO ITS STIFFNESS AS A BEAM

The approximate methods already given apply strictly to struts for which $I = Cx^2$, and with slight error, to other forms. In general, the ultimate strength of a relatively slender strut varies with its stiffness. In order to show how nearly the ultimate strength of a strut is proportional to its stiffness as a beam, we will calculate the deflection of some tapered struts, supported at the ends and loaded at the middle.

Using the method of internal work,

$$U = \int \frac{M^2}{2EI}\, dx,$$

in which $U$ is the work and $M$ is the bending moment. For a beam supported at the ends and loaded at the middle, with the origin at a distance $a$ to the left of the left end,

$$M = \frac{P}{2}(x - a).$$

$$U = \int \frac{P^2}{8EI}(x-a)^2\, dx = \frac{P^2}{8EC}\int \left(1 - \frac{2a}{x} + \frac{a^2}{x^2}\right) dx$$

$$U = \frac{P^2}{8EC}\cdot\left[x - 2a \log\left(\frac{x}{a}\right) - \frac{a^2}{x}\right]_a^{ka},$$

for one-half the beam. For the entire beam

$$U = \frac{P^2 a}{4EC}(k - \frac{1}{k} - 2 \log k).$$

The external work is $\frac{P}{2} y_{max}$. Equating the two expressions for work,

$$y_{max} = \frac{Pa}{2EC}\cdot(k - \frac{1}{k} - 2 \log k).$$

Substituting $\frac{P}{EC}=\frac{PL^2}{4EI_2\left(1-\frac{1}{k}\right)^2}$ and $a=\frac{L}{2\ (k-1)}$,

$$y_{max}=\frac{P\ L^3\ k^2}{16EI_2\ (k-1)^3}\ (k-\frac{1}{k}-2\log k).$$

The deflection at the middle of a beam of uniform section, having moment of inertia $I_2$ is

$$y_{max}=\frac{PL^3}{48EI_2},$$

if the beam is supported at the ends and loaded at the middle. Since stiffness is inversely proportional to the deflection due to equal loads, the relative stiffness is given by

$$\text{relative stiffness}=\frac{(k-1)^3}{3k^2\ (k-\frac{1}{k}-2\ \log\ k)}.$$

For the case in which $k=4$ and $\sqrt{\frac{1}{k}}=0.5$,

$$\text{relative stiffness}=\frac{27}{48\ (4-0.25-2\times 1.38629)}=0.577.$$

The stiffness of a beam with this taper is 58 per cent of that of a uniform beam of the same length and maximum moment of inertia. From Table 8 it is seen that the strength ratio for this value of $k$ is 0.49.

The fourth column of Table 8 gives a series of stiffness ratios. These are somewhat higher than the corresponding strength ratios, and the difference is greater in the struts of large taper.

These computations are for struts for which $I=Cx^2$, which approximates the form of actual struts, except that the surfaces of the two halves meet at a slight angle at the middle, instead of on a common tangent. A formula was derived for struts having the equation $I=I_2-Cx^2$, in which $x$ is the distance from the middle. This strut has the desired form at the middle, but converges more slowly near the middle and more rapidly near the ends than the actual struts. The calculations show higher strength ratios and stiffness ratios than those for the struts of Table 8. The stiffness ratios exceed the strength ratios in about the same proportion in both cases.

To find approximately the strength of any tapered strut, support it at the ends as a beam, apply a light load at the middle, and measure the deflection $y_{max}$. From the equation of a uniform beam,

$$y_{max} = \frac{PL^3}{48EI},$$

calculate the equivalent $EI$. Substitute this value of $EI$ in Euler's formula to get the ultimate strength. The result will be somewhat too great, since the stiffness ratio exceeds the strength ratio.

For greater accuracy test a uniform strut of the same material of cross section equal to that at the middle of the tapered strut. From the two deflections get the stiffness ratio and make the corresponding relative correction in the value of $EI$. The loads and deflections must be small so as not to injure the strut.

*Example.*—A tapered strut 5 feet long supported at the ends is deflected 0.060 inch at the middle by a load of 10 pounds at the middle.

$$EI = \frac{10 \times 60^3}{48 \times 0.060} = 750\,000$$

Suppose a uniform beam of the same length is deflected 0.042 inch by the same load. The stiffness ratio is $\frac{42}{60} = 0.70$. Interpolating from Table 8, the corresponding strength ratio is found to be 0.62. The corrected value of the equivalent $EI$ is

$$750\,000 \times \frac{62}{70} = 660\,000.$$

Instead of measuring the deflection of a uniform strut, the value of $\left(\frac{I_1}{I_2}\right)^{\frac{1}{4}}$ may be calculated from the dimensions of the strut and used in Table 8 to find the relation of strength ratio to stiffness ratio.

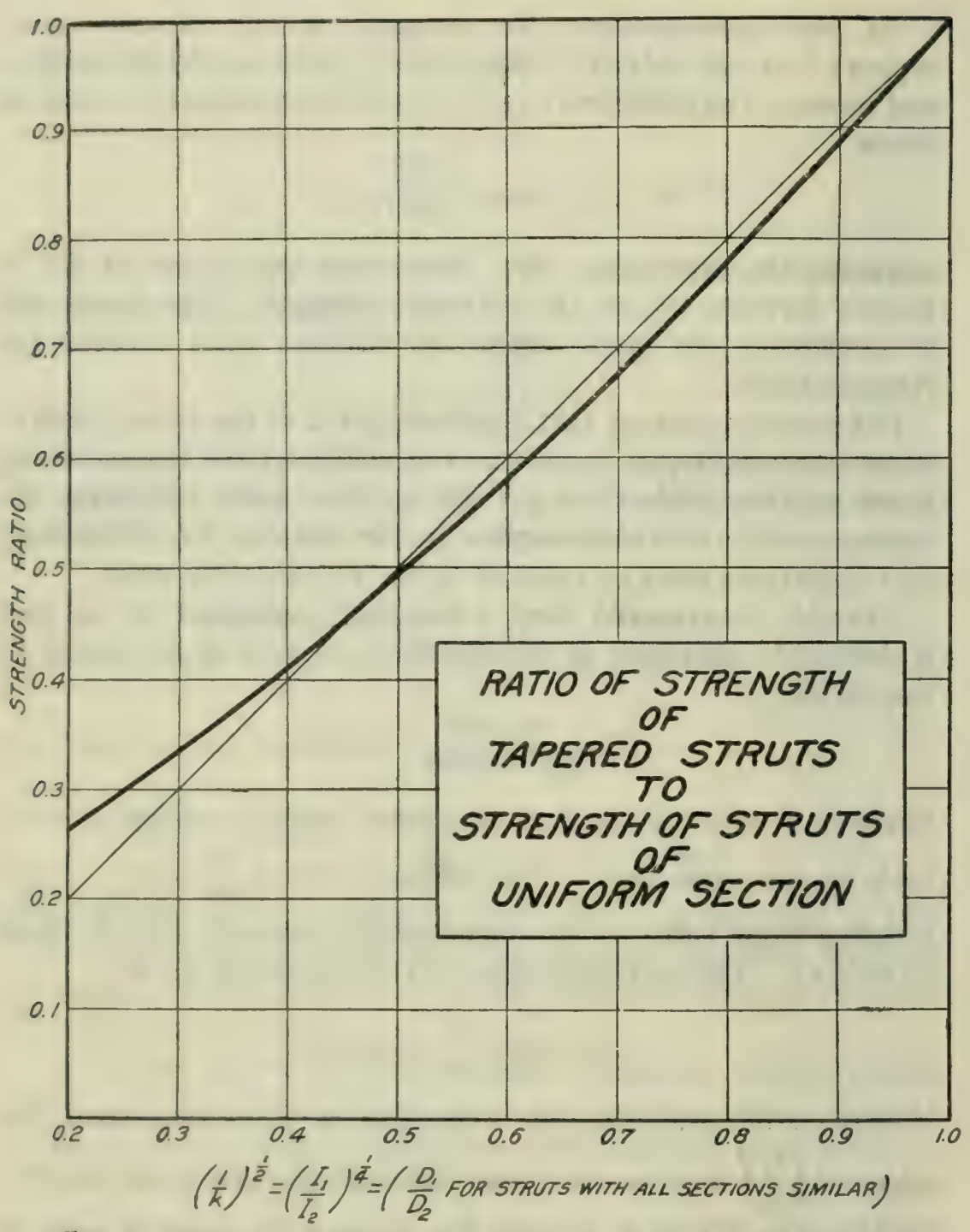


FIG. 14.—*Comparison of strength of tapered struts and struts of uniform section*

**TABLE 1.—Compression Test Square-End Strut B–4, Tested Aug. 20, 1917, by J. E. B.**

[Length, 4 feet 2½ inches; breadth, 1.738 inches; depth, 1.762 inches. Slenderness ratio, 100. Compression with 30-inch Howard gages placed 2.75 inches apart. Counterweight of 9 pounds at each end of gages. Deflection measurements taken with Johnson dials.]

| Unit stress, pounds per square inch | Compression, inches | | | | | | Average unit compression, inch per inch | Deflection, inches | |
|---|---|---|---|---|---|---|---|---|---|
| | North gage | | | South gage | | | | | |
| | At gage | At surface | | At gage | At surface | | | Up | South |
| | | In 30 inches | Per inch | | In 30 inches | Per inch | | | |
| I | II | III | IV | V | VI | VII | VIII | IX | X |
| 200 | 0.0000 | 0.00000 | 0.000000 | 0.0000 | 0.00000 | 0.000000 | 0.000000 | 0.000 | 0.000 |
| 400 | .0049 | .00465 | .000155 | .0036 | .00384 | .000128 | .000142 | .004 | .003 |
| 600 | .0090 | .00873 | .000291 | .0075 | .00777 | .000259 | .000275 | .009 | .003 |
| 800 | .0122 | .01189 | .000396 | .0105 | .01081 | .000360 | .000378 | .009 | .004 |
| 1000 | .0163 | .01595 | .000632 | .0144 | .01475 | .000492 | .000512 | .010 | .005 |
| 1200 | .0201 | .01961 | .000654 | .0174 | .01789 | .000596 | .000625 | .012 | .007 |
| 1400 | .0245 | .02390 | .000797 | .0212 | .02180 | .000727 | .000762 | .013 | .009 |
| 1600 | .0284 | .02767 | .000922 | .0244 | .02513 | .000838 | .000880 | .013 | .012 |
| 1800 | .0330 | .03215 | .001072 | .0283 | .02915 | .000972 | .001022 | .013 | .015 |
| 2000 | .0372 | .03618 | .001206 | .0316 | .03262 | .001087 | .001147 | .013 | .018 |
| 2200 | .0414 | .04015 | .001338 | .0345 | .03475 | .001192 | .001265 | .020 | .021 |
| 2400 | .0461 | .04466 | .001489 | .0382 | .03964 | .001321 | .001405 | .021 | .021 |
| 2600 | .0510 | .04927 | .001642 | .0415 | .04323 | .001441 | .001541 | .021 | .030 |
| 2800 | .0563 | .05414 | .001804 | .0444 | .04656 | .001552 | .001678 | .022 | .036 |
| 3000 | .0611 | .05897 | .001952 | .0472 | .04973 | .001658 | .001805 | .022 | .043 |
| 3100 | .0639 | .06105 | .002035 | .0482 | .05105 | .001702 | .001868 | .024 | .048 |
| 3200 | .0683 | .06495 | .002165 | .0499 | .05324 | .001775 | .001970 | .025 | .056 |
| 3400 | .0742 | .07002 | .002334 | .0512 | .05538 | .001846 | .002090 | .029 | .071 |
| 3500[a] | .0810 | .07560 | .002520 | .0513 | .05670 | .001890 | .002205 | .033 | .089 |
| 3446 | | | | | | | | .045 | .113 |
| 3560 | | | | | | | | .048 | .122 |
| 3634 | | | | | | | | .055 | .146 |
| 3725[b] | | | | | | | | | |
| 3520[c] | | | | | | | | .120 | .275 |
| 3447[d] | | | | | | | | .455 | .271 |

[a] Removed Howard gages and counterweights. Load dropped to 3446 pounds per square inch.

[b] Maximum load. Continued to deflect south with compression head stationary.

[c] Cracking noise. Strut bent up and south.

[d] Compression failure, 1.5 inches from middle.

## TABLE 2.—Compression Test Square-End Strut C–4, Tested Aug. 17, 1917, by J. E. B.

[Length, 5 feet 3⅛ inches; breadth, 1.738 inches; depth, 1.763 inches. Slenderness ratio, 125. Tested on large Emery machine. Compression measured with 30-inch Howard gages placed 2.75 inches apart. Counterweights of 9 pounds at each end of gages. Deflection measurements taken with Johnson dials.

| Unit stress, pounds per square inch | Compression, inches | | | | | | Average unit compression, inch per inch | Deflection, inches | |
|---|---|---|---|---|---|---|---|---|---|
| | North gage | | | South gage | | | | | |
| | At gage | At surface | | At gage | At surface | | | Up | South |
| | | In 30 inches | Per inch | | In 30 inches | Per inch | | | |
| I | II | III | IV | V | VI | VII | VIII | IX | X |
| 200 | 0.0000 | 0.00000 | 0.00000 | 0.0000 | 0.00000 | 0.00000 | 0.00000 | 0.000 | 0.000 |
| 400 | .0038 | .00380 | .00127 | .0038 | .00380 | .00127 | .00127 | .002 | .000 |
| 600 | .0075 | .00740 | .00247 | .0070 | .00710 | .00237 | .00242 | .005 | .000 |
| 800 | .0114 | .01133 | .00378 | .0110 | .01107 | .00369 | .00373 | .006 | .000 |
| 1000 | .0146 | .01449 | .00483 | .0140 | .01411 | .00470 | .00477 | .006 | .000 |
| 1200 | .0186 | .01845 | .00615 | .0178 | .01795 | .00598 | .00607 | .011 | .000 |
| 1400 | .0222 | .02211 | .00737 | .0217 | .02179 | .00726 | .00732 | .011 | .000 |
| 1600 | .0252 | .02502 | .00834 | .0242 | .02438 | .00813 | .00823 | .011 | .000 |
| 1800 | .0296 | .02935 | .00978 | .0282 | .02845 | .00948 | .00963 | .012 | .003 |
| 2000 | .0333 | .03305 | .01102 | .0319 | .03215 | .01072 | .01087 | .013 | .005 |
| 2200 | .0379 | .03754 | .01251 | .0359 | .03626 | .01209 | .01230 | .013 | .005 |
| 2400 | .0412 | .04084 | .01361 | .0392 | .03954 | .01316 | .01340 | .015 | .005 |
| 2600 | .0456 | .04513 | .01504 | .0430 | .04347 | .01449 | .01477 | .016 | .004 |
| 2700 | .0471 | .04668 | .01556 | .0448 | .04522 | .01507 | .01532 | .019 | .004 |
| 2800 | .0494 | .04896 | .01632 | .0470 | .04744 | .01561 | .01607 | .020 | .004 |
| 2900 | .0510 | .05067 | .01689 | .0492 | .04953 | .01651 | .01670 | .022 | .004 |
| 3000 | .0524 | .05240 | .01747 | .0522 | .05220 | .01740 | .01743 | .024 | .004 |
| 3100 [a] | .0520 | .05320 | .01773 | .0586 | .05740 | .01913 | .01843 | .022 | .028 |

[a] Removed gages and counterweights. Load dropped to 2840 pounds per square inch. Strut suddenly bent upward and continued to bend with reduced load. Compression failure, 1 inch from middle at bottom and one side.

**TABLE 3.—Summary of Tests of Square-End Struts**

| Strut | Length | Breadth | $\frac{L}{r}$ | Depth | $\frac{L}{r}$ | Area | Modulus of elasticity | Proportional limit | Ultimate unit load |
|---|---|---|---|---|---|---|---|---|---|
| | Inches | Inches | | Inches | | Inches$^2$ | Lbs./in.$^2$ | Lbs. in.$^2$ | Lbs. in.$^2$ |
| A-1 | 12.625 | 1.745 | 25.1 | 1.765 | 24.8 | 3.08 | 1 840 000 | 2800 | 5000 |
| E-2 | 12.625 | 1.736 | 25.2 | 1.745 | 25.1 | 3.03 | 1 670 000 | 1400 | 4191 |
| C-3 | 12.625 | 1.745 | 25.1 | 1.765 | 24.8 | 3.08 | 1 870 000 | 2000 | 4026 |
| D-4 | 12.625 | 1.742 | 25.1 | 1.762 | 24.8 | 3.07 | 1 530 000 | 2200 | 4400 |
| E-5 | 12.625 | 1.742 | 25.1 | 1.775 | 24.6 | 3.09 | 1 400 000 | 2800 | 5227 |
| A-6 | 12.625 | 1.746 | 25.0 | 1.735 | 25.2 | 3.03 | 1 830 000 | 4000 | 5809 |
| C-5 | 12.625 | 1.757 | 24.9 | 1.733 | 25.3 | 3.04 | 1 690 000 | 1800 | 4375 |
| E-6 | 12.625 | 1.750 | 25.0 | 1.753 | 25.0 | 3.07 | 1 730 000 | 2800 | 5472 |
| Average | | | | | | | | | 4812 |
| C-2 | 25.250 | 1.726 | 50.7 | 1.731 | 50.5 | 2.99 | 1 650 000 | 2200 | 4047 |
| D-3 | 25.250 | 1.745 | 50.1 | 1.756 | 49.8 | 3.06 | 1 700 000 | 2000 | 4248 |
| E-4 | 25.250 | 1.744 | 50.2 | 1.764 | 49.6 | 3.08 | 1 760 000 | 2800 | 4383 |
| A-5 | 25.250 | 1.737 | 50.4 | 1.765 | 49.6 | 3.07 | 1 600 000 | 3200 | 4723 |
| B-6 | 25.250 | 1.753 | 49.9 | 1.755 | 49.8 | 3.08 | 1 350 000 | 2800 | 5032 |
| Average | | | | | | | | | 4487 |
| C-1 | 37.875 | 1.750 | 75.0 | 1.732 | 75.8 | 3.03 | 1 140 000 | 1600 | 3164 |
| E-3 | 37.875 | 1.745 | 75.2 | 1.766 | 74.3 | 3.08 | 1 500 000 | 1800 | 3743 |
| A-4 | 37.875 | 1.740 | 75.4 | 1.758 | 74.7 | 3.06 | 1 390 000 | 2200 | 3400 |
| B-5 | 37.875 | 1.737 | 75.8 | 1.772 | 74.0 | 3.08 | 1 860 000 | 2600 | 4580 |
| C-6 | 37.875 | 1.747 | 75.1 | 1.748 | 75.1 | 3.05 | 1 400 000 | 2400 | 3734 |
| B-2a | 37.875 | 1.723 | 76.1 | 1.722 | 76.2 | 2.97 | 1 770 000 | 2200 | 4417 |
| B-2b | 37.875 | 1.761 | 74.6 | 1.732 | 75.8 | 3.05 | 1 480 000 | 2600 | 4764 |
| C-3 | 37.875 | 1.755 | 74.8 | 1.738 | 75.5 | 3.05 | 1 680 000 | 2200 | 4033 |
| Average | | | | | | | | | 3979 |
| D-1 | 50.500 | 1.732 | 101.0 | 1.746 | 100.2 | 3.02 | 1 180 000 | 1800 | 2748 |
| E-2 | 50.500 | 1.735 | 100.6 | 1.729 | 101.2 | 3.00 | 1 600 000 | 2100 | 3300 |
| A-3 | 50.500 | 1.768 | 98.7 | 1.744 | 100.3 | 3.08 | 1 600 000 | 2400 | 3864 |
| B-4 | 50.500 | 1.738 | 100.7 | 1.762 | 99.3 | 3.06 | 1 560 000 | 2600 | 3725 |
| D-6 | 50.500 | 1.745 | 100.2 | 1.765 | 99.1 | 3.08 | 1 540 000 | 2600 | 3815 |
| Average | | | | | | | | | 3490 |
| E-1 | 63.125 | 1.734 | 126.0 | 1.754 | 124.7 | 3.04 | 1 140 000 | 1600 | 2100 |
| A-2 | 63.125 | 1.736 | 126.0 | 1.752 | 124.8 | 3.04 | 1 770 000 | 2000 | 2960 |
| B-3 | 63.125 | 1.770 | 123.6 | 1.743 | 125.5 | 3.09 | 1 650 000 | 2200 | 2913 |
| C-4 | 63.125 | 1.738 | 125.8 | 1.763 | 124.0 | 3.06 | 1 640 000 | 2600 | 3100 |
| D-5 | 63.125 | 1.738 | 125.8 | 1.763 | 124.0 | 3.06 | 1 820 000 | 1800 | 2931 |
| Average | | | | | | | | | 2801 |
| E-1 | 75.750 | 1.735 | 151.2 | 1.746 | 150.3 | 3.03 | 800 000 | 1000 | 1200 |
| A-2 | 75.750 | 1.738 | 151.0 | 1.758 | 149.2 | 3.06 | 1 720 000 | 1500 | 1993 |
| B-3 | 75.750 | 1.762 | 148.9 | 1.746 | 150.3 | 3.08 | 1 720 000 | 2000 | 2259 |
| D-5 | 75.750 | 1.738 | 151.0 | 1.748 | 150.1 | 3.03 | 1 520 000 | 1750 | 2178 |
| E-6 | 75.750 | 1.750 | 150.0 | 1.754 | 149.6 | 3.07 | 1 710 000 | 2200 | 2279 |
| Average | | | | | | | | | 1974 |

**TABLE 3.—Summary of Tests of Square-End Struts—Continued**

| Strut | Length | Breadth | $\frac{L}{r}$ | Depth | $\frac{L}{r}$ | Aera | modulus of elasticity | Proportional limit | Ultimate unit load |
|---|---|---|---|---|---|---|---|---|---|
| | Inches | Inches | | Inches | | Inches | Lbs./in. | Lbs./in. | Lbs./in$^2$ |
| D–1 | 88.375 | 1.733 | 176.6 | 1.743 | 175.5 | 3.02 | 940 000 | 900 | 1109 |
| E–2 | 88.375 | 1.765 | 175.5 | 1.742 | 175.7 | 3.07 | 1 600 000 | 1300 | 1539 |
| B–4 | 88.375 | 1.741 | 175.8 | 1.762 | 173.7 | 3.07 | 1 740 000 | 1200 | 1750 |
| C–5 | 88.375 | 1.729 | 177.1 | 1.758 | 174.1 | 3.04 | 1 870 000 | 1550 | 1891 |
| D–6 | 88.375 | 1.739 | 176.0 | 1.746 | 175.3 | 3.04 | 1 360 000 | 1100 | 1530 |
| Average | | | | | | | | | 1564 |
| C–1 | 101.000 | 1.741 | 201.0 | 1.731 | 202.1 | 3.01 | 1 100 000 | 600 | 900 |
| D–2 | 101.000 | 1.737 | 201.4 | 1.747 | 200.3 | 3.03 | 1 600 000 | 700 | 1155 |
| E–3 | 101.000 | 1.749 | 200.0 | 1.760 | 198.7 | 3.08 | 1 600 000 | 1150 | 1299 |
| A–4 | 101.000 | 1.742 | 200.8 | 1.757 | 199.1 | 3.06 | 1 730 000 | 1200 | 1454 |
| B–5 | 101.000 | 1.732 | 202.0 | 1.758 | 199.0 | 3.05 | 1 680 000 | 1200 | 1230 |
| C–6 | 101.000 | 1.742 | 200.8 | 1.753 | 199.6 | 3.05 | 1 550 000 | 1050 | 1210 |
| Average | | | | | | | | | 1210 |
| B–1 | 113.625 | 1.735 | 226.9 | 1.748 | 225.2 | 3.03 | 1 240 000 | 700 | 891 |
| C–2 | 113.625 | 1.730 | 227.4 | 1.735 | 226.9 | 3.00 | 1 720 000 | 800 | 1100 |
| D–3 | 113.625 | 1.752 | 224.8 | 1.744 | 225.7 | 3.06 | 1 640 000 | 700 | 1013 |
| E–4 | 113.625 | 1.742 | 226.0 | 1.757 | 224.0 | 3.06 | 1 740 000 | 900 | 1003 |
| A–5 | 113.625 | 1.741 | 226.1 | 1.758 | 223.8 | 3.06 | 1 580 000 | 800 | 1029 |
| B–6 | 113.625 | 1.747 | 225.4 | 1.751 | 224.8 | 3.06 | 1 360 000 | 900 | 1000 |
| Average | | | | | | | | | 1006 |
| A–1 | 126.250 | 1.742 | 251.1 | 1.767 | 247.6 | 3.08 | 1 600 000 | 850 | 873 |
| B–2 | 126.250 | 1.736 | 252.0 | 1.741 | 251.2 | 3.02 | 1 600 000 | 600 | 950 |
| C–3 | 126.250 | 1.761 | 248.4 | 1.737 | 251.8 | 3.06 | 1 520 000 | 600 | 915 |
| D–4 | 126.250 | 1.744 | 250.8 | 1.768 | 247.4 | 3.08 | 1 680 000 | 500 | 900 |
| E–5 | 126.250 | 1.745 | 250.7 | 1.768 | 247.4 | 3.08 | 1 560 000 | 600 | 871 |
| Average | | | | | | | | | 902 |

## TABLE 4.—Bending Tests of Spruce

| Test piece | Fiber stress $S$ from curve at deflection of 0.2 inch | Depth $d$ | Modulus of elasticity | Modulus of rupture |
|---|---|---|---|---|
| | Lbs./in.² | Inches | Lbs./in.² | Lbs./in.² |
| B–1 | 5900 | 1.743 | 1 625 000 | 8600 |
| D–2 | 5770 | 1.769 | 1 544 000 | 8000 |
| A–3 | 5600 | 1.765 | 1 523 000 | 6300 |
| C–4 | 5900 | 1.750 | 1 625 000 | 8600 |
| C–5 | 5400 | 1.732 | 1 496 000 | 7600 |
| E–6 | 4720 | 1.778 | 1 274 000 | 7200 |

## TABLE 5.—Compression Test of Round-End Strut E–9

[Tested Aug. 24, 1917, by J. E. B. and L. J. L. Length, 6 feet 3¾ inches; breadth, 1.742 inches; depth, 1.752 inches. Slenderness ratio, 150. Tested on large Emery machine. Compression measured with 30-inch Howard gages. Counterweight of 9 pounds at each end of gages. Deflection measurements taken with Johnson dials.]

Zero correction at end of test, 30 pounds. Ultimate load 3050−30=3020 pounds=990 pounds per square inch.

| Total load, pounds | Unit load, pounds per square inch | Compression in 30 inches, inches | | Average unit compression, inches per inch | Deflection, inches | |
|---|---|---|---|---|---|---|
| | | North gage | South gage | | Down | North |
| 305 | 100 | 0.0000 | 0.0000 | 0.000000 | 0.000 | 0.000 |
| 610 | 200 | .0011 | .0011 | .000037 | .000 | .000 |
| 915 | 300 | .0020 | .0027 | .000078 | .001 | .000 |
| 1220 | 400 | .0034 | .0041 | .000125 | .004 | .002 |
| 1525 | 500 | .0049 | .0050 | .000165 | .009 | .003 |
| 1677 | 550 | .0054 | .0058 | .000187 | .014 | .004 |
| 1830 | 600 | .0061 | .0063 | .000207 | .017 | .004 |
| 2060 | 675 | .0071 | .0069 | .000233 | .022 | .004 |
| 2135 | 700 | .0074 | .0073 | .000245 | .024 | .004 |
| 2287 | 750 | .0080 | .0078 | .000263 | .032 | .004 |
| 2440 | 800 | .0089 | .0088 | .000295 | .039 | .003 |
| 2593 | 850 | .0100 | .0096 | .000327 | .051 | .002 |
| 2745 | 900 | .0111 | .0103 | .000357 | .079 | .001 |
| 2898 | 950 | .0120 | .0110 | .000383 | .103 | .011 |
| 3050 | 1000 | .0140 | .0131 | .000452 | .312 | .015 |
| 3050 | 1000 | .0156 | .0147 | .000505 | .482 | .029 |
| 3300[a] | ..... | ..... | ..... | ..... | .537 | .039 |
| 2969[b] | 974 | ..... | ..... | ..... | .612 | .039 |
| 3025 | 992 | ..... | ..... | ..... | .862 | .069 |
| 3015 | 989 | ..... | ..... | ..... | 1.142 | ..... |

[a] Removed gages. Load stood at 1750 pounds total.

[b] Removed counterweights. Load stood at 2950 pounds.

**TABLE 6.—Summary of Tests of Round-End Struts**

| Strut | Length | Breadth | Depth | $\frac{L}{r}$ | Area | Modulus of elasticity | Proportional limit | Ultimate unit load |
|---|---|---|---|---|---|---|---|---|
| | Inches | Inches | Inches | | Inches$^2$ | Lbs./in.$^2$ | Lbs./in.$^2$ | Lbs./in.$^2$ |
| C-7 | 12.625 | 1.774 | 1.748 | 25.0 | 3.10 | 1 690 000 | 2400 | 4226 |
| D-8 | 12.625 | 1.765 | 1.748 | 25.0 | 3.08 | 1 950 000 | 2500 | 4314 |
| E-9 | 12.625 | 1.741 | 1.745 | 25.0 | 3.04 | 3 300 000 | 2400 | 5487 |
| Average | | | | | | | | 4676 |
| C-7 | 25.250 | 1.783 | 1.751 | 50.0 | 3.12 | 1 560 000 | 2000 | 3630 |
| D-8 | 25.250 | 1.760 | 1.750 | 50.0 | 3.08 | 1 750 000 | 2800 | 3610 |
| E-9 | 25.250 | 1.746 | 1.752 | 50.0 | 3.06 | 2 100 000 | 2800 | 4908 |
| Average | | | | | | | | 4049 |
| C-7 | 37.875 | 1.768 | 1.752 | 74.9 | 3.10 | 1 820 000 | 2400 | 2816 |
| D-8 | 37.875 | 1.754 | 1.754 | 74.8 | 3.08 | 1 600 000 | 2600 | 2607 |
| E-9 | 37.875 | 1.749 | 1.755 | 74.8 | 3.07 | 2 430 000 | 3800 | 3905 |
| Average | | | | | | | | 3109 |
| A-7 | 50.500 | 1.807 | 1.750 | 100.0 | 3.16 | 1 680 000 | 1200 | 1503 |
| B-8 | 50.500 | 1.752 | 1.748 | 100.1 | 3.06 | 1 920 000 | 1800 | 1938 |
| C-9 | 50.500 | 1.738 | 1.747 | 100.1 | 3.04 | 2 200 000 | 1400 | 2031 |
| Average | | | | | | | | 1824 |
| B-7 | 63.125 | 1.788 | 1.750 | 125.0 | 3.13 | 1 560 000 | 800 | 1065 |
| C-8 | 63.125 | 1.756 | 1.752 | 124.8 | 3.08 | 1 640 000 | 1000 | 1117 |
| D-9 | 63.125 | 1.742 | 1.750 | 125.0 | 3.05 | 2 240 000 | 1400 | 1437 |
| Average | | | | | | | | 1206 |
| C-7 | 75.750 | 1.786 | 1.756 | 149.4 | 3.13 | 1 760 000 | 770 | 772 |
| D-8 | 75.750 | 1.773 | 1.755 | 149.5 | 3.11 | 1 380 000 | 500 | 592 |
| E-9 | 75.750 | 1.742 | 1.752 | 149.8 | 3.05 | 2 380 000 | 800 | 990 |
| Average | | | | | | | | 785 |
| B-7 | 88.375 | 1.795 | 1.753 | 174.7 | 3.15 | 1 880 000 | 550 | 640 |
| C-8 | 88.375 | 1.768 | 1.755 | 174.4 | 3.10 | 1 440 000 | 460 | 503 |
| D-9 | 88.375 | 1.731 | 1.752 | 174.8 | 3.03 | 2 520 000 | 680 | 743 |
| Average | | | | | | | | 629 |
| A-7 | 101.000 | 1.708 | 1.752 | 199.7 | 2.99 | 1 600 000 | 360 | 441 |
| B-8 | 101.000 | 1.769 | 1.750 | 200.0 | 3.09 | 1 460 000 | 320 | 354 |
| C-9 | 101.000 | 1.730 | 1.750 | 200.0 | 3.03 | 2 100 000 | 360 | 521 |
| Average | | | | | | | | 439 |

**TABLE 7.—Computations for Determining the Value of $k$ for Use in Plotting the Curve of Fig. 14**

| $\frac{4P}{EC}$ | $\sqrt{\frac{4P}{EC}-1}=\tan\alpha$ | $\alpha$ deg | Log $\alpha$ deg | Log 2$\alpha$ radians | Log tan$\alpha$ | Log log$_e k$ | Log log$_{10} k$ | Log $k$ |
|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 135.00 | 2.13033 | 0.67324 | 0.00000 | 0.67324 | 0.31102 | 2.04650 |
| 5 | 2 | 116.57 | 2.06659 | .60950 | .30103 | .30847 | 1.94625 | .88359 |
| 10 | 3 | 108.43 | 2.03515 | .57806 | .47712 | .10094 | 1.73672 | .54793 |
| 26 | 5 | 101.31 | 2.00565 | .54856 | .69897 | 1.84959 | 1.48737 | .30717 |
| 101 | 10 | 95.71 | 1.98096 | .52387 | 1.00000 | 1.52387 | 1.16165 | .14510 |
| 626 | 25 | 92.29 | 1.96515 | .50806 | 1.39794 | 1.11012 | 2.74790 | .05596 |
| 10001 | 100 | 90.57 | 1.95700 | .49990 | 2.00000 | 2.49990 | 2.13769 | .01373 |

| Log $\frac{1}{k}$ | $\frac{1}{k}$ | $\left(1-\frac{1}{k}\right)$ | Log $\left(1-\frac{1}{k}\right)^2$ | Log $\frac{4P}{EC}$ | Log $\frac{4P}{EC}\left(1-\frac{1}{k}\right)^2$ | Log strength ratio | Strength ratio | $\sqrt{\frac{1}{k}}$ |
|---|---|---|---|---|---|---|---|---|
| 3.95350 | 0.0090 | 0.9910 | 1.99215 | 0.30103 | 0.29318 | 1.29888 | 0.1990 | 0.0948 |
| 1.11641 | .1307 | .8693 | 1.87834 | .69897 | .57731 | 1.58301 | .3828 | .3616 |
| 1.45207 | .2832 | .7168 | 1.71080 | 1.00000 | .71080 | 1.71650 | .5206 | .5322 |
| 1.69283 | .4930 | .5070 | 1.41002 | 1.41497 | .82499 | 1.83069 | .6772 | .7021 |
| 1.85490 | .7160 | .2840 | 2.90664 | 2.00432 | .91096 | 1.91666 | .8254 | .8462 |
| 1.94404 | .8791 | .1209 | 2.16485 | 2.79657 | .96142 | 1.96712 | .9271 | .9376 |
| 1.98627 | .9689 | .0311 | 4.98552 | 4.00004 | .98556 | 1.99126 | .9801 | .9843 |

**TABLE 8.—Ratios of Moment of Inertia and Strength Ratios**

| $\sqrt{\frac{1}{k}}$ | Ratio of $I$ at $\frac{L}{3}$ to $I_2$ | Ratio of $I$ at $\frac{5L}{16}$ to $I_2$ | Ratio of stiffness of tapered beam to that of uniform beam | Strength ratio |
|---|---|---|---|---|
| 0.2 | 0.46 | 0.41 | 0.40 | 0.27 |
| .3 | .48 | .44 | .44 | .34 |
| .4 | .52 | .47 | .51 | .41 |
| .5 | .56 | .52 | .58 | .49 |
| .6 | .62 | .58 | .65 | .58 |
| .7 | .69 | .65 | .73 | .67 |
| .8 | .77 | .75 | .81 | .77 |
| .9 | .88 | .86 | .90 | .88 |

WASHINGTON, April 19, 1919.

DEPARTMENT OF COMMERCE

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S. W. STRATTON, DIRECTOR

No. 153

## AREA MEASUREMENT OF LEATHER

BY

FREDERICK J. SCHLINK, Associate Physicist

*Bureau of Standards*

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By Frederick J. Schlink

CONTENTS


| | Page |
|---|---|
| I. Introduction—Importance of the subject | 3 |
| II. Types of area-measuring machines used in the leather trade | 8 |
| 1. The pin machine | 9 |
| 2. The wheel machine | 13 |
| (*a*) Principles of operation | 13 |
| (*b*) Typical designs | 14 |
| (1) Chain and lever totalizing gear | 14 |
| (2) Differential gear totalizing system | 17 |
| (*c*) Sources and determination of errors | 19 |
| (1) Spacing of wheels | 19 |
| (2) Width of rim | 19 |
| (3) Overrun of wheelwork | 22 |
| (4) Effect of thickness of material | 28 |
| (5) Variance due to imperfections of the linkwork | 30 |
| (6) Secular changes in hides and skins | 35 |
| III. Methods of testing leather-measuring machines | 35 |
| 1. Form and material of the area standard | 35 |
| 2. Determination of machine performance | 42 |
| 3. Acknowledgements | 46 |
| IV. Summary | 46 |


## I. INTRODUCTION—IMPORTANCE OF THE SUBJECT

In January, 1917, the Bureau of Standards, at the instance of the commissioner of weights and measures of the Commonwealth of Massachusetts, undertook the investigation of the methods and machines employed in the leather industry in the area measurement of hides and skins. Owing to the short time and limited staff available for the work, it was impossible to carry out the complete and exhaustive study of the field that its commercial importance would warrant. At the entrance of the United States into the war in April, 1917, the whole of the staff and facilities of the Bureau were devoted to military work, which precluded all but the briefest and most cursory consideration of the problem from that time until the end of 1918. Important and suggestive data were obtained, however, and some of these results are here presented as of possible utility in relation to further studies which may

be undertaken, and of service in guiding designers and users of leather-measuring machines in their choice of mechanisms and methods. As leather-measuring machines do not enter into direct relationship with the ultimate consumer, their operation has, in general, not been given the close supervision by weights and measures officials that is accorded the more common trade measuring instruments, such as weighing scales, capacity measures, and the like. On this account, up to the time of the investigations reported in the present paper, no complete and suitable procedure for conducting tests of leather-measuring machines had been developed; no tolerances were used, nor had any comparative study of types been made.

The literature of this subject is very meager. The best material available up to the time of the investigation by the Bureau is to be found in "The Manufacture of Leather," by Davis.[1] The first edition of this book devotes a chapter of 12 pages to the subject of leather-measuring machines, including 13 figures and a list of United States patents issued in the interval 1790–1883, inclusive. The material of this chapter is almost entirely descriptive, covering both obsolete and existing types of leather-measuring machines. No information is given as to the performance possibilities or comparative operating accuracies of the different types.

In the 1897 edition of the above-named work the space devoted to leather-measuring machines is reduced to four and one-half pages by the elimination of a considerable amount of material descriptive of obsolete or undeveloped types of leather-measuring machines. In this edition, only two illustrations are given, one of a typical wheel machine and one of a pin machine. On account of the scarcity of satisfactory illustrations of leather-measuring machines, both of these are reproduced in the present paper. Like the chapter in the earlier edition, the later treatment by Davis gives no information beyond descriptions of the machines and the manufacturers' claims for them. No adequate data of the sort required by the designer nor any indication of the sources and types of error to be expected are given.

A pamphlet, "Suggestions to Sealers," issued by the department of weights and measures of the Commonwealth of Massachusetts, includes five pages regarding leather-measuring machines, comprising brief descriptions of the hand rack, the pin, wheel, and power machines, with suggestions regarding certain tests to be applied.

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[1] Henry Carey Baird & Co., Philadelphia, 1885; 2d ed., 1897.

The results of the Bureau's investigation, as comprised in the author's reports, were promptly and regularly forwarded to the Massachusetts commissioner of weights and measures, and by him transmitted to various representatives of the National Boot & Shoe Manufacturers' Association and the National Tanners' Association. The former association published in the report of the meeting of its executive committee of April 23, 1917, an extended report made by the Bureau of Standards under date of March 30, 1917, "On Certain Principles in the Design of Leather-Measuring Machines," which included a discussion of the principles of operation of the pin machine and the wheel machine, and an analysis of the sources of error of the latter, including the width of tires, spacing of wheels, overrun of wheelwork, effect of thickness of leather measured, and lost motion in the transference chains. The same association also distributed leaflets comprising the report of February 5, "On the Form and Material of Standards of Area for Testing Purposes," and that of February 12, which gives the results of an extended test upon which are based a great many of the conclusions regarding the serious inaccuracy of existing types of machines in service. The basis of this test was the measurement upon five different machines of five different calfskins ranging in area from 8.4 to 14.5 square feet. Readings were taken for each of these skins on each of the five machines, and the following tabular comparison was made with the actual areas of the five skins as determined by careful planimetric measurements conducted in the laboratories of the Bureau, careful correction being made for the shrinkage of the skins between the time of their measurement by the five measuring machines and their subsequent measurement by planimeter at the Bureau. This study also gave valuable data upon the effect of the overrun of wheelwork in occasioning serious errors of reading in excess.

Some information as to the serious difficulties met with in connection with these machines, as known to members of the leather trade, will be found in the January 18, 1917, and January 17, 1918, issues of the Shoe and Leather Reporter (Boston). In the earlier article indication is given as to the amount of variation in measurement which is commonly found in the service operation of the usual measuring machines. The comparative measurements made upon the five different machines using five different skins, as referred to above, fully confirmed these opinions, and showed that, of the five machines investigated, the average errors ex-

tended over the wide range of 4.4 per cent in excess to 0.1 per cent in deficiency.

**TABLE 1.—Recapitulation of Comparative Results on Test of Five Leather-Measuring Machines, January, 1917**

| Serial number and actual area of skins (planimeter) | Readings of machine "A" | | | | Readings of machine "B" | | | |
|---|---|---|---|---|---|---|---|---|
| | First reading | Second reading | Average of first and second reading | Reading at very low speed | First reading | Second reading | Average of first and second reading | Reading at very low speed |
| 1: 12.40 | 12.87 | 13.06 | 12.96 | 12.35 | 12.45 | 12.50 | 12.48 | 12.35 |
| 2: 8.88 | 9.22 | 9.20 | 9.21 | 8.80 | 8.75 | 8.80 | 8.78 | 8.65 |
| 3: 14.46 | 14.87 | 14.90 | 14.88 | 14.35 | 14.40 | 14.55 | 14.48 | 14.40 |
| 4: 8.36 | 8.80 | 8.65 | 8.72 | 8.22 | 8.35 | 8.35 | 8.35 | 8.37 |
| 5: 12.59 | 13.35 | 13.50 | 13.42 | 12.58 | 12.90 | 12.85 | 12.88 | 12.80 |
| Totals: 56.69 | ..... | ..... | 59.19 | 56.30 | ..... | ..... | 56.97 | 56.57 |
| Error of machine | ..... | ..... | +2.50 | −.39 | ..... | ..... | +.28 | −.12 |
| Per cent error | ..... | ..... | +4.4 | −.7 | ..... | ..... | +.5 | −.2 |

| Serial number and actual area of skins (planimeter) | Readings of machine "C" | | | | Readings of machine "D" | | | Readings of machine "E" | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | First reading | Second reading | Average of first and second reading | Reading at very low speed | First reading | Second reading | Average of first and second reading | First reading | Second reading | Average of first and second reading |
| 1: 12.40 | 12.45 | 12.40 | 12.42 | 12.30 | 12.70 | 12.75 | 12.72 | 12.30 | 12.45 | 12.38 |
| 2: 8.88 | 9.05 | 8.95 | 9.00 | 8.80 | 8.95 | 8.80 | 8.88 | 8.90 | 8.80 | 8.85 |
| 3: 14.46 | 14.60 | 14.65 | 14.62 | 14.30 | 14.63 | 14.68 | 14.66 | 14.38 | 14.48 | 14.43 |
| 4: 8.36 | 8.45 | 8.40 | 8.42 | 8.20 | 8.50 | 8.50 | 8.50 | 8.50 | 8.40 | 8.45 |
| 5: 12.59 | 12.75 | 12.60 | 12.67 | 12.55 | 12.80 | 12.80 | 12.80 | 12.55 | 12.55 | 12.55 |
| Totals: 56.69 | ..... | ..... | 57.13 | 56.15 | ..... | ..... | 57.56 | ..... | ..... | 56.66 |
| Error of machine | ..... | ..... | +.44 | −.54 | ..... | ..... | +.87 | ..... | ..... | −.03 |
| Per cent error | ..... | ..... | +.8 | −.9 | ..... | ..... | +1.5 | ..... | ..... | −.1 |

NOTE.—Areas are in square feet. A plus (+) error corresponds to a reading in excess; a minus (−) error corresponds to a reading in deficiency.

The very great commercial importance of the problem can be indicated by the statement—for which the National Boot & Shoe Manufacturers' Association and the National Tanners' Association are the authorities—that the leather annually measured upon an area basis in this country amounts to 900 000 000 square feet, worth $450 000 000. All finished leather, including boot and shoe uppers, book, enameled, and upholstery leather, are sold upon an area basis, and such hides and skins all have their selling price determined by the use of leather-measuring machines. In fact, a single machine may determine the selling price of several

million dollars' worth of hides per annum. One such machine, tested during this investigation and found to have a large error in excess, determined the sale of about $2 000 000 worth per annum, and this large volume is believed to be no very unusual circumstance, since in a large leather warehouse in another city a business of $8 000 000 per annum was being handled on two and occasionally three machines. Moreover, the unit value of the leather may be very high—$1.50 per square foot or even more. The Boot & Shoe Manufacturers' Association, in one of the reports referred to above, has stated that 3 per cent variations of measurement are common. This statement becomes the more significant when it is recalled that practically this means that 3 per cent errors are common, as the investigations have shown that the variations of leather-measuring machines are almost without exception in the direction of excess measurement and the variations, therefore, distribute themselves all in the one direction from accurate measurement.

At this writing, also, the question of leather measurement is becoming prominent in England, and it is reported [2] that the standardization of the superficial measurement of leather has been discussed with the Board of Trade by a deputation representing the Federation of Curriers and Light Leather Tanners, and the Federation of Boot & Shoe Manufacturers, the former group representing the sellers and the latter the buyers. It appears that at the present time no law is in force in England by which dishonest measurement can be punished, and that little information is available regarding leather-measuring machines, while many users of such machines have no means of verifying their accuracy. The consumption of leather purchased by measurement in England is stated to be approximately 400 000 000 square feet per annum. Reference was made to the importance of protecting English buyers against inaccurately measured leather imported from abroad. Some discussion was given to the importance of the use of a template of the correct substance for carrying out tests and of adjusting the machine when changing the substance of the goods being measured. The speed of the machine was also mentioned as being important, and the statement made that the slow speed "will tend to show greater surface than when the leather is rushed through," which is, of course, an error of statement so far as our knowledge of the conditions can determine, the effect of high-speed operation

[2] Leather Trades' Review, Mar. 26, 1919; The Leather Manufacturer, May, 1919.

being just the reverse according to our own experiments. Attention is called to the discrepancies due to shrinkage after glazing or laying in store.

The writer has just had opportunity to read the brief discussion of the leather-measurement question which appears in the annual reports of the Director of the British National Physical Laboratory, 1913–1915, which, may be briefly abstracted as follows:

Under the direction of Mr. Attwell and at the joint request of the Board of Trade and the Federation of Light Leather Trades, an investigation into the behavior and accuracy of power-driven area-measuring machines has been undertaken, and machines in daily use tested at intervals. The secular variation in circular rubber templates, used for testing the machines, has been investigated, and attempts have been made to age such templates artificially.

The investigation begun in 1913 was referred to in the succeeding annual report as having been completed, and the conclusions briefly stated therein. The first was that "the machine should be controlled by means of reliable and suitable templates which should be of approximately the same area and thickness as the skins under measurement." It appears from theoretical considerations that errors from 0.16 to 0.32 square foot must be tolerated with the different machines in use, although the errors found in practice exceeded the above figures, due largely to the fact that none of the machines was fully controlled by suitable templates. Reference is made to the necessity of providing in addition to the machine tolerance, an allowance to cover the shrinkage of the skins. It is stated that "it would appear to be impossible at present for a buyer to substantiate a claim against a seller in which the error on an individual skin did not exceed one-half square foot, or in which the mean error on a consignment did not exceed one-fourth square foot per skin. These figures might be reduced to about one-half by the use of an improved type of machine.

The shrinkage of area templates made of rubber fabrics is again discussed, and shown to amount to as much as 1 per cent in 15 months in laboratory storage, and in some cases templates which have been used in the field show shrinkage amounting to nearly 2 per cent, most of which occurs in the early life of the template, suggesting artificial aging as a remedy.

So far as the number of leather-measuring machines in use is concerned, practically no data are available. We are informed, however, that about 200 such machines of all types were in use in Massachusetts alone at the beginning of 1917.

## II. TYPES OF AREA-MEASURING MACHINES USED IN THE LEATHER TRADE

The types of leather-measuring machines known in the leather trade are four:

1. The hand frame—which is nothing but a screen divided into squares comprising one-fourth of square foot each, which is a superposed upon the hide to be measured and by counting of the included squares—affords a means of estimating the area to some degree of acuracy, depending upon the skill of the user. This

simple device is very little used at the present time because of its slowness and lack of precision, and the fact that it requires superior skill on the part of the measurer.

2. The pin machine, which provides for the weighing of a number of vertical rods or pins, the remaining pins in the group being relieved of communication with the weighing mechanism by the interposition of the hide being measured.

3. The wheel machine, which is the power-driven type now in most common use, and which performs the function of measurement by the traversing of the hide under a bank of uniformly spaced narrow wheels whose several rotations due to the passage of the hide are then mechanically totalized.

4. The planimeter, of which one or two special types of large capacity are available for the measurement of hides and skins. The planimeter, of course, gives a reading of area by manually tracing the outline or perimeter of the hide.

The present use of the planimeter, it is believed, is limited to very few instances, and it practically does not enter into the commercial measurement of hides and skins, but only into the determination of unit costs as involved in the number of shoe elements which can be cut from a known area. The planimeter will also be useful in standardization work, as in checking area standards used in the testing of ordinary leather-measuring, machines and, possibly, for the routine measurement of high-priced leather; its utility for the latter purpose depends upon a study of the economics of the operation, the cost of measurement being offset against the cost of the errors which may characterize competing instruments for the same purpose.

### 1. THE PIN MACHINE

The pin machine, which is no longer manufactured but of which a few examples built 25 years ago or more are still in operation, is illustrated in Figs. 1 and 2, and its construction and operation are as follows: A frame is supported pivotally by a knife-edge at the rear, and is so counterbalanced as to be lifted easily into and out of parallelism with the table upon which, in the first illustration, it is seen to rest. A part of the frame is connected by a cord to the load-supporting system of a suspended spring balance suitably hung in position above the table and the inclinable frame. The frame is made up of light wooden strips perforated at uniform intervals, and arranged in lines parallel to the plane of the spring balance seen in the illustration. Through each of the perforations

a metal pin passes, loosely projecting some distance beyond the lower surface of the frame, and prevented from dropping through by an eye or head at its upper end. The table over which the frame is supported is made up as a grid of wooden strips perpendicular to the plane of the spring scale. The spacing of the bars in the grid is such that the pins coming through the frame above pass into the interstices and do not touch the grid itself. The lower ends of all the pins thus pass into the slots formed in the table, and all stand at the same level.

Thus, when all the pins are hanging through the slots in the table as described, their weight is carried by the suspended frame, supported in part by the pivot on which that frame turns and in part by the spring balance to which its front bar is connected. The spring balance, therefore, is in equilibrium under the load, and in this position may be said to register zero area. If, now, the frame is raised, a sheet of leather placed upon the table or grid, and the frame again lowered, so that it is parallel and close to the table though not in contact with it, those pins below which a portion of the leather is lying will be raised by it and will slide upwardly through the holes in the inclinable frame in such manner that their weight is no longer carried by it, as their weight is now received and supported by the leather rather than by the ring or head from which they are normally hung. There are thus some pins which are supported by the inclinable frame from the shouldered portion at their upper ends (the ring or head mentioned above), and some are supported by the leather, which lifts the shouldered portion out of contact with the inclinable frame by contact with their lower ends. The frame being thus relieved of the weight of the latter group of pins, the spring balance will change its reading in direct proportion to the number of pins which no longer pass into the slots of the grid but are supported by the leather, the pins being so proportioned that their weight varies inversely as their distance from the pivot about which the frame turns, so that each pin exercises the same turning effort about that fulcrum. This adjustment is accomplished by making the pins of the various rows of decreasing length and diameter, as may be convenient to gain the desired weight gradation. The spring balance, being graduated in units of area in a reverse direction from the ordinary weight graduation, gives increasing readings of area for what corresponds to decreasing values of weight of the pins supported by the frame. Simple means for changing the weight or turning moment of the inclinable frame are provided so that the

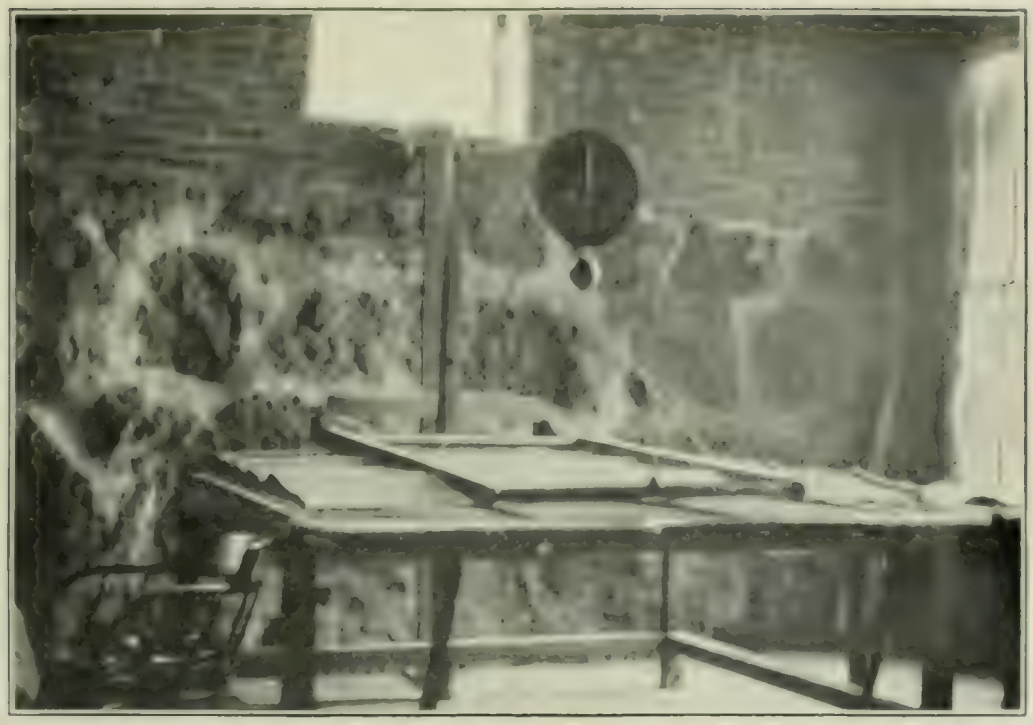

FIG. 1

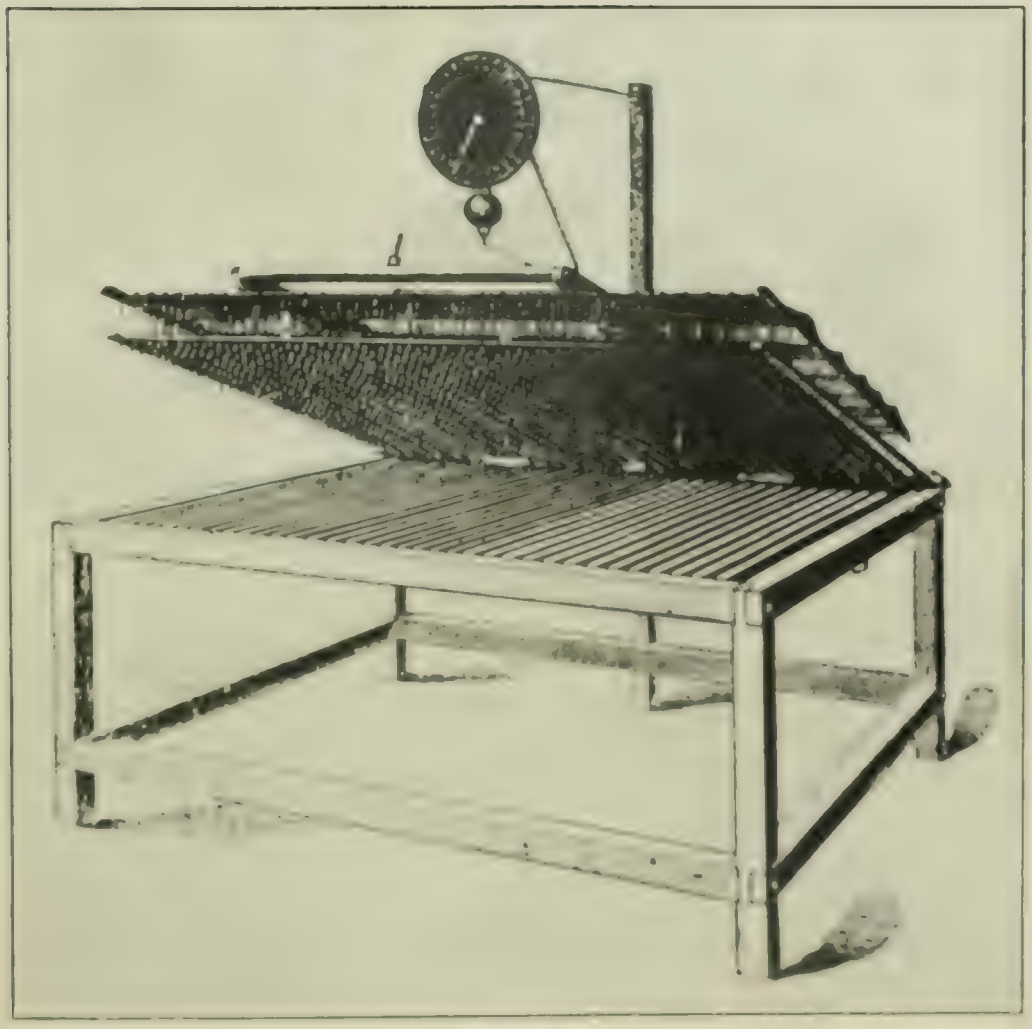

FIG. 2

scale may be made to indicate a zero reading when the pins all hang through the slots in the grid below—that is, when no leather is in place for measurement.

Obviously, if the number of pins could be indefinitely large (or, conversely, their spacing indefinitely close) an exact determination of the area to be measured would be obtainable in this way, were it not for the friction which would be introduced at the points where the pin slides against the guiding holes in the supporting frame. The degree of approximation thus increases with the closeness of the spacing of the pins in the frame. On machines of this type which were examined during the investigation, the spacing of the pins was for some unknown reason different in the two perpendicular directions, being 2 inches in a direction parallel to the plane of the spring balance shown and 1 ½ inches in the direction perpendicular to this plane. In practice, the friction of the pins passing through the frame, though they were very numerous, appeared to be so small as to be negligible, and no difficulty was had in obtaining readings which appeared to be quite free from errors due to this cause, as the spring balance would oscillate quite freely and for a considerable time after the frame was lowered to the table.

It would seem that if a well-constructed weighing scale is used, this type of machine should offer the possibility of very satisfactory accuracy when the pins are closely spaced. The use of a spring balance is no way essential, as almost any desired type of weighing scale can be employed for indicating the change in the weight carried by the frame.

In the book by Davis, above referred to, a machine having a similar essential principle of operation is described, but it is not known to what extent this type of machine came into use. It is the invention of Williams, Moore, and Hulburt, in 1879, and the weighing of the pins is carried out by the reception of their lower ends upon a weighing scale platform mounted below what corresponds to the grid or table described above. Under this system the pins which pass through and are not supported by the leather are allowed to exercise their effect upon the weighing scale, and the result is read upon a dial as in the device described in greater detail above. In this case, as before, the weight indicated corresponds directly to the area which is not covered by the leather, the reduction to area of leather being carried out by a reverse scale of graduations, as has been indicated. This machine is equipped with a sort of brake designed to check the oscillations of the weigh-

ing system before the reading is taken. It should be noted that in this type of construction, the pins do not touch the holes through which they pass, at the moment when the weighing operation is being performed, as in this position the pins are left resting free of their guiding holes, supported upright by flat end surfaces, either on the surface of the leather or on the surface of the weighing table below it; moreover, in this machine the pins are not required to vary in weight but are all uniform, as the system on which they are weighed is a true weighing scale having a platform moving parallel to its initial position instead of rotating about a fixed point. The indications are therefore independent of the position of the applied load.

The author has often heard the statement that the pin machine is inaccurate for the reason that it is subject to variations due to changes in the atmospheric humidity, temperature, etc., as affecting the dimensions of the wooden frame. As a matter of fact, this defect, the importance of which has doubtless been overestimated, is not peculiar to this type of machine but to the materials of its construction, and can be made quite negligible by the use of other material for the framework. In fact, it would be quite possible to use a metal framework having a small or negligible coefficient of expansion, so that the apparatus would be even less affected by temperature changes than are the existing types of wheel machines.

The advantages of the pin machine are obvious. It is simple in construction, cheap to manufacture (its cost should not exceed one-third to one-half of that of the wheel machines), it affords possibilities of very satisfactory accuracy when a sufficiently large number of pin elements are used, and it eliminates, moreover, many of the sources of error common to the wheel machines as, for example, that due to overrun of wheelwork, that due to the width of tires (the analogous error is of no moment in the pin machine, since the area of the ends of the pins can be very small), and that due to the thickness of the leather. The disadvantages principally raised in objection to this type of machine are, first, that it is slow in operation; and, second, that it does not take account of the area involved in the concavity or bellying of the hide.

So far as the first objection goes, it is believed to be overdrawn. The author, in a few observations made without special preparation, upon the use of the pin machine in comparison with the wheel machine, each in the hands of an experienced operator,

found that the former required not more than 30 per cent more time per skin than the latter (pin machine, 12 seconds per skin; wheel machine, 9 seconds per skin); this despite the fact that the wheel machine was clearly overspeeded, as were most of the wheel machines observed. (See under Overrun of Wheelwork, below. As explained more fully in that section, any rational comparison of the speed of operation of the two types will require that the wheel machine be operated at a speed known to be low enough that the overrun error does not exceed a suitable small tolerance.) An item in a Peabody, Mass., newspaper refers to a competitive trial between the pin machine and the wheel machine, and actually credits a higher speed of operation to the former.

### 2. THE WHEEL MACHINE

(*a*) PRINCIPLES OF OPERATION.—The wheel machines operate upon a different principle, which may be briefly described by reference to the appended sketch (Fig. 3) representing any desired

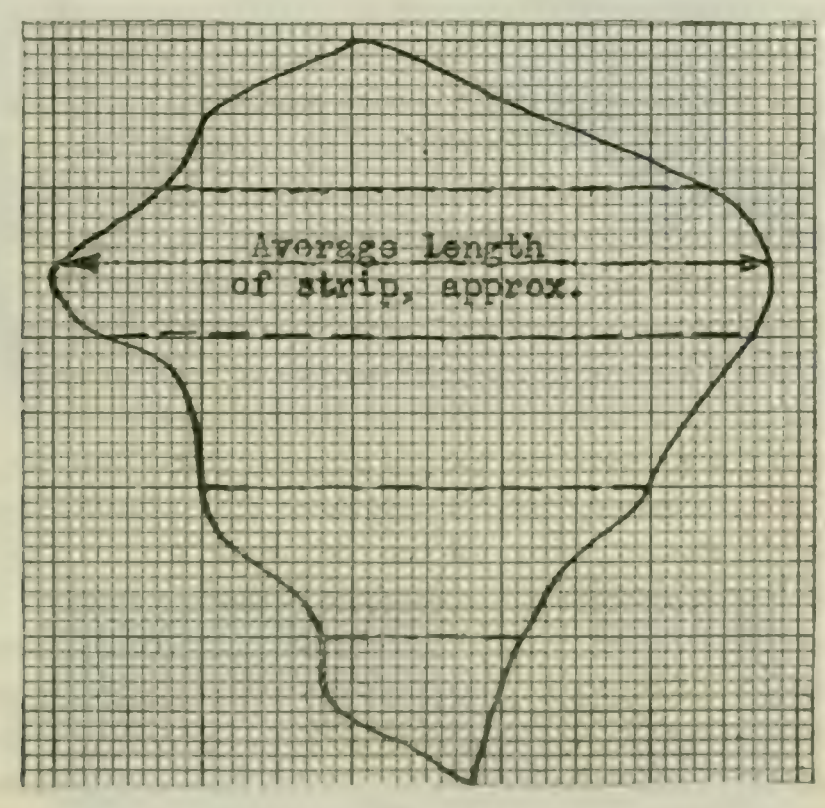


FIG. 3

irregular area. Imagine that parallel lines be drawn upon such an area dividing it into strips of uniform width The area of each strip will then be given by the product of its width into its average length and the area of the whole figure by the common width of the strips multiplied by the sum of the lengths of all the

strips. Now, if the irregularities of the outline to be measured are not marked by sharp discontinuities, the average length of each strip is determined approximately by the length of its middle line or median, and it is upon this assumption that the operation of the wheel-type machine is based. The measurement is carried out mechanically somewhat upon the following principle: The irregular area to be measured is drawn through the machine by a feed-roll, the construction being such that the leather in its passage produces rotation of the members of a series of parallel, uniformly spaced wheels when, and only when, leather is in contact with and passing under such wheels. Each wheel, therefore, rotates through an angle which is proportional to the length of the middle line of the strip which extends on each side of that wheel a distance equal to half the space between the wheels. If now, the rotations of the several wheels are totalized and that sum is multiplied by a constant, the result will be in units of area, and will represent an approximate integration of the irregular figure measured.

(*b*) TYPICAL DESIGNS.—(*1*) *Chain and Lever Totalizing Gear.*—In the actual construction of the wheel machine, an old model of which is shown in front elevation in Fig. 4 and in transverse section in Fig. 5, the roller *B*, which extends the full working length of the machine, rotates continuously clockwise. The wheels, *A*, which are the uniformly spaced, parallel wheels referred to above, rotate by frictional engagement with *B*, a small clearance being allowed between the pinion affixed to the axis of *A* and the segmental gear, *C*. If, now, a hide be inserted between *B* and *A*, wheel *A* is slightly lifted, the axis of *B* being fixed, and the pinion affixed to *A* at once engages the segment *C*, causing *C* to rotate clockwise until the extremity of the strip over which *A* is passing has passed out from between *A* and *B*. At this instant *A* drops back into contact with *B* and the pinion on *A* is thereby disengaged from *C*, whereupon the pawl seen in the figure prevents retrograde rotation of *C*. Segment *C*, then, in each case describes an arc proportional to the length of the median of the corresponding strip of the hide.

The travel of the several segments *C* (or in some cases complete gears, performing an identical function) is totalized by a system of chains passing over pulleys mounted on levers, the lever system being so arranged that the contribution of motion due to the winding up of individual chains on the drums affixed to the center of the

FIG. 4

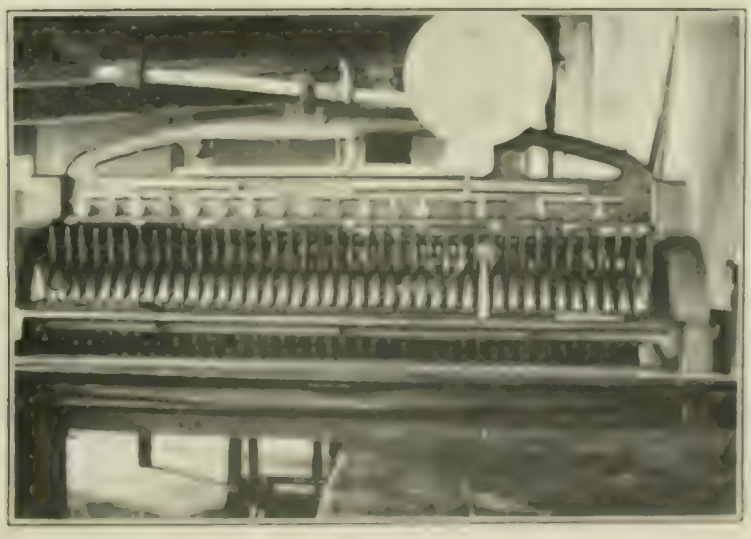

FIG. 7

segments $C$, is transmitted in reduced amount, but in equal reduction for every chain, to a single rack or segmental gear $f^1$ driving

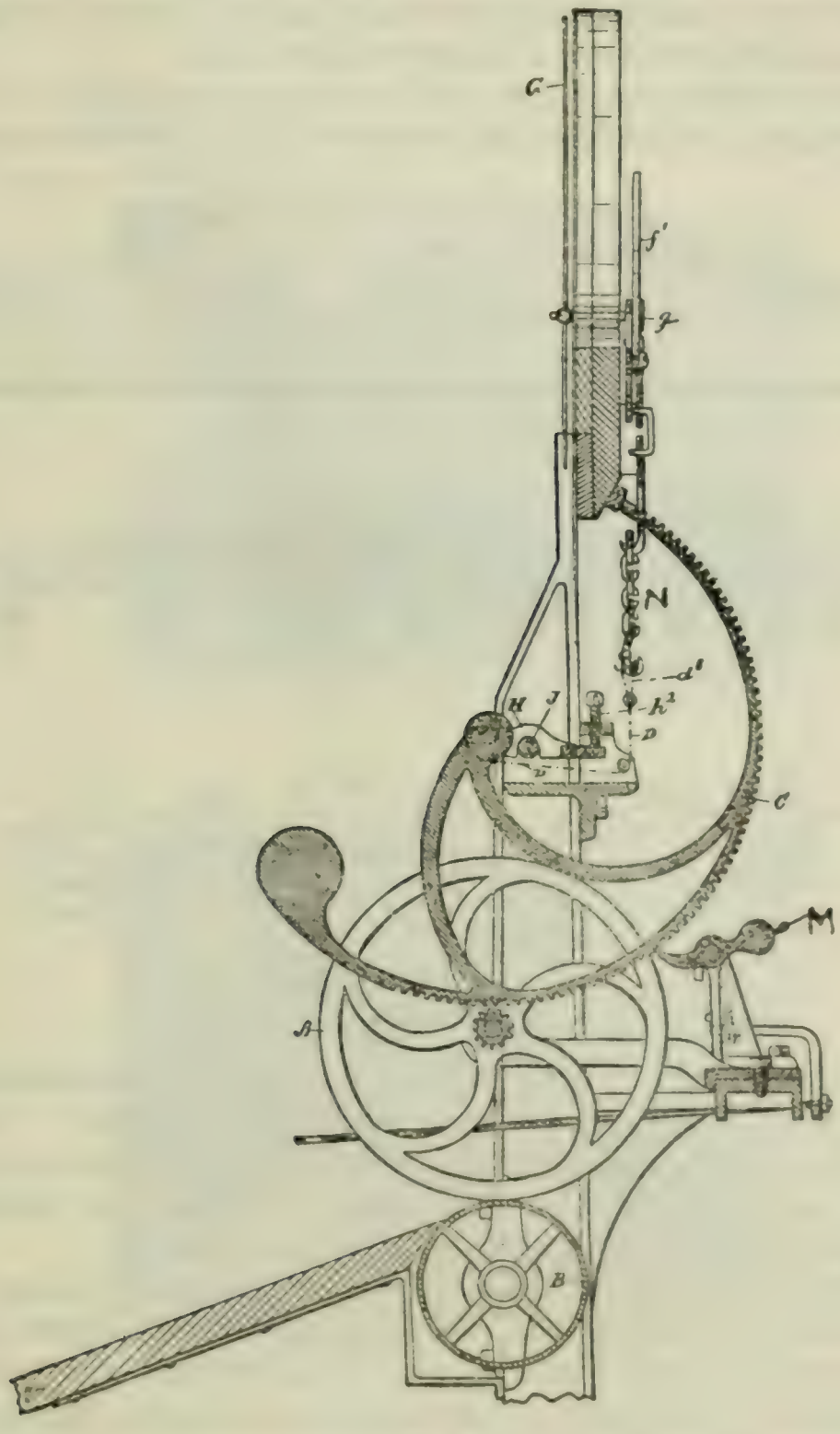


FIG. 5

*A*, traversing wheel carrying at its center the traversing wheel pinion; *B*, feed roll; *C*, accumulating segment (or gear); *M*, pawl restraining retrograde movement of *C* until machine is zeroized by lifting all pawls; and *N*, transference chain.

the pinion of the indicator at which the reading is obtained. In brief, then, the lengths of the several parallel medians of the irregu-

lar area are measured individually by the rotation of uniformly spaced wheels, and the amount of motion of these several wheels is totalized by a suitable lever system and, finally, through a suitable rack and pinion movement, registered upon a dial.

The next figure shows a typical lever system by which the uniform reduction of displacements is carried out. It will be observed

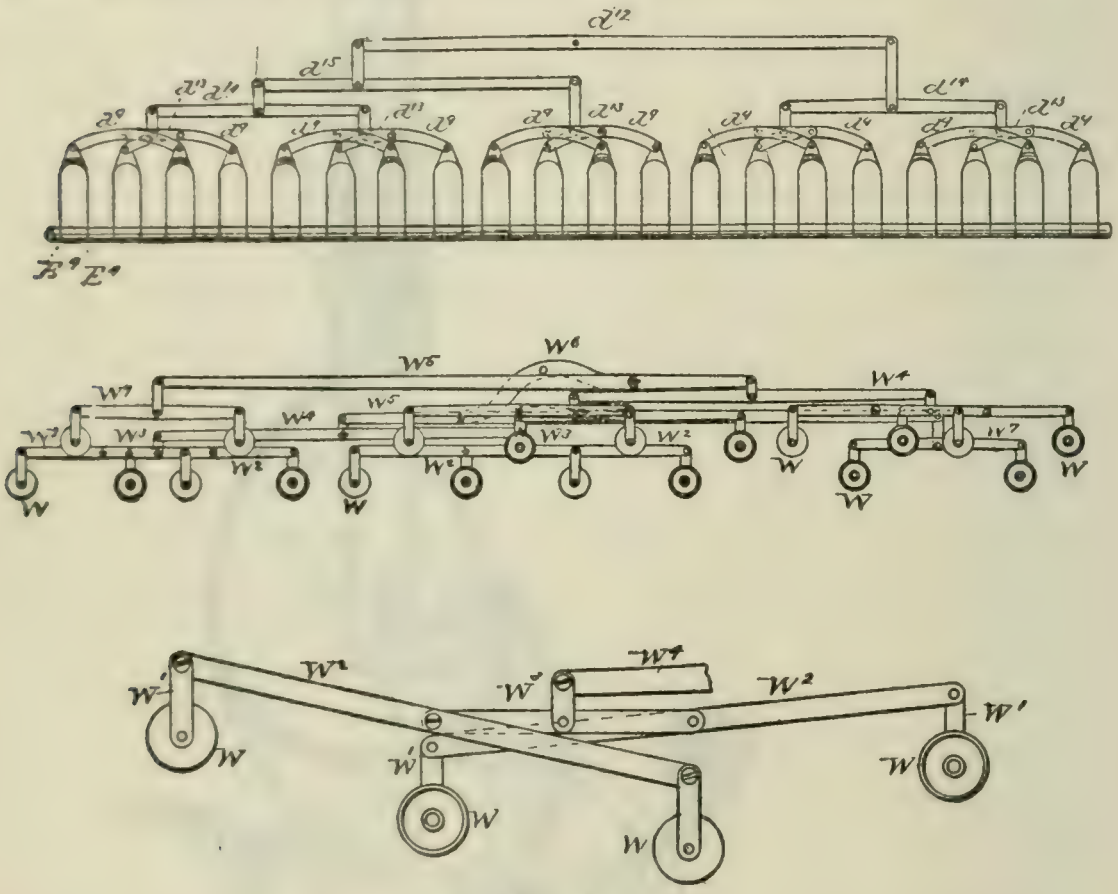

FIG. 6

that this leverage is so arranged as to produce the same reduction of movement of any chain when measured at the point $d^{12}$. Detail dimensions of the lever system by which this end is obtained need not be cited, as a suitable arrangement can always be designed upon the well-known principles of the simple lever.

When it is desired to reset the pointer to zero to permit the measurement of another skin, a bar engaging all of the pawls above mentioned is operated, disengaging the pawls from contact with the segments and permitting the segments to return to their lowermost position, propelled by their own unbalanced weight. Leather bumpers are usually included to assure uniform and shockless stoppage of the segments, as they return to their zero position. Machines of this type are usually graduated to 30 square feet by increments of one-eighth or one-fourth of a square foot. A few machines have a capacity of 60 square feet by one-fourth of a square foot.

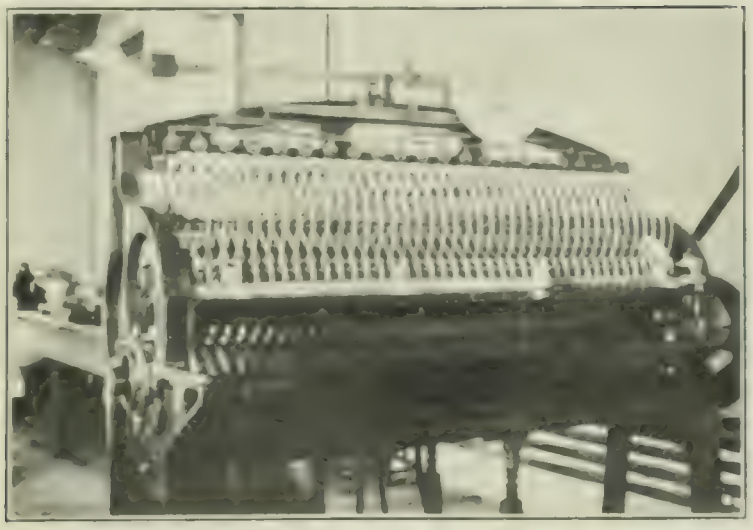

FIG. 8

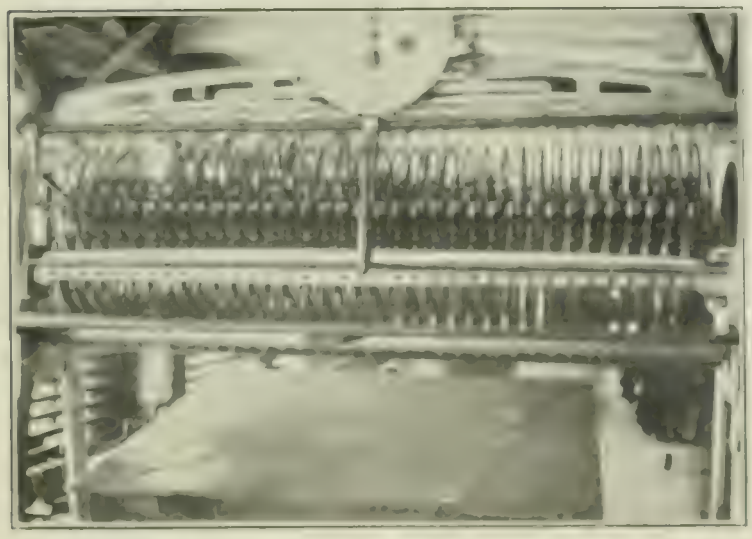

FIG. 9.—*Typical sheet type leather measuring machines*

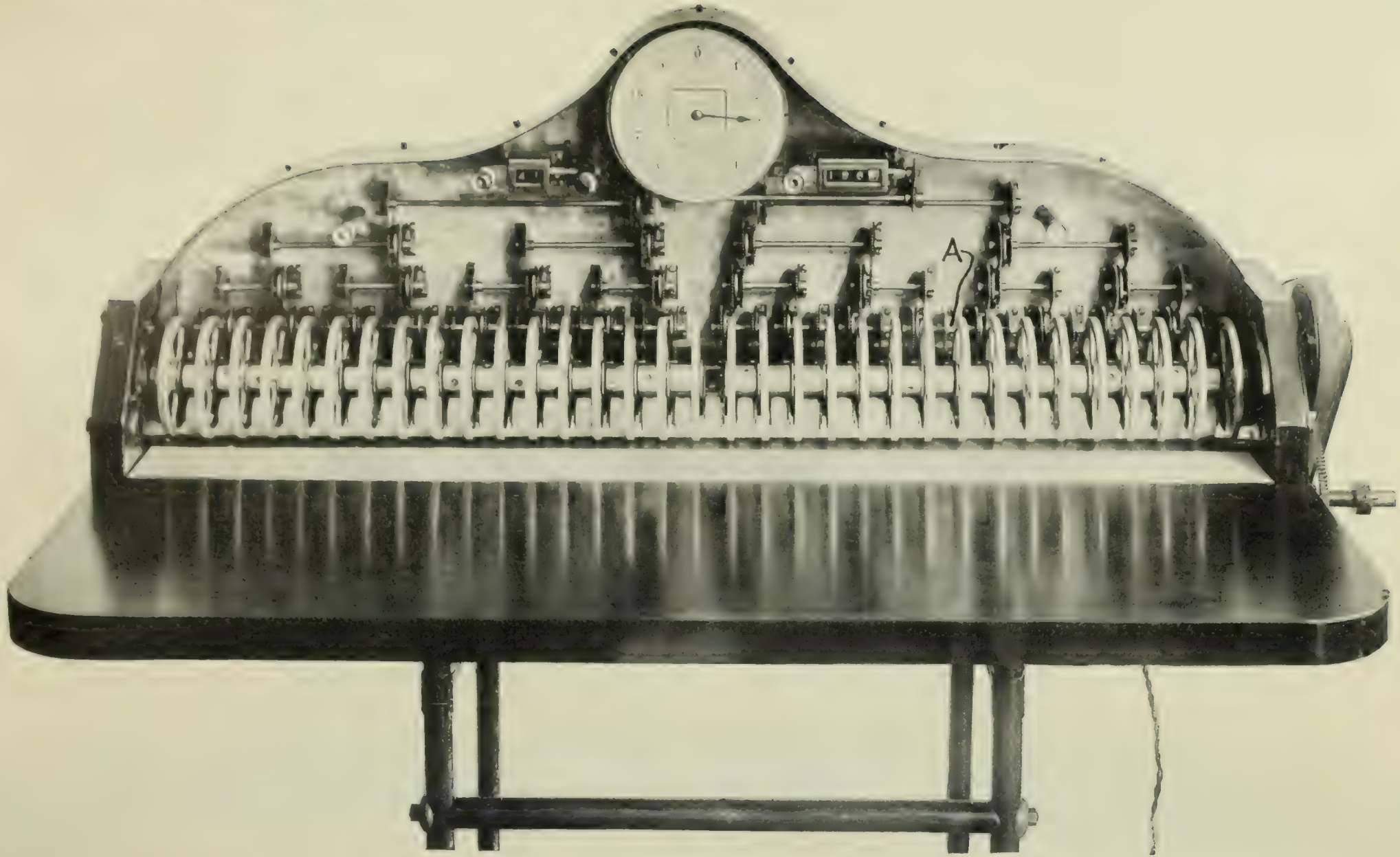


FIG. 10

In another design, operating upon this same general principle, the segments, *C*, are extended to full circles with teeth over the whole circumference. Instead of permitting these wheels to revert to the initial position, the machine is zeroized by unclutching the winding drums at the centers of these gears and restoring the drum itself to its initial position. This method is designed to eliminate the wear of the segmental gears used in the other type, which is, of course, greatest at the portions of the circumference near the initial position of engagement. The use of continuous forward rotation of the accumulating gears is, however, associated with a disadvantage, in that the use of a balanced gear definitely aggravates the error due to overrun of wheelwork, as will appear in the later discussion.

(*2*) *Differential Gear Totalizing System.*—Another type of totalizing train only recently developed and not yet ready for the market is based upon the principle of differential gearing. The appended Fig. 10 illustrates the arrangement used in an early model of this machine. Eack measuring wheel is pivoted between a pair of narrow-tired disks which are rotated by the feed roller, and serve to smooth and direct the skin as it passes through. As in the machines using the chain-and-lever totalizing gear, the measuring wheels rise at the entrance of the skin, due to its thickness, and thereby effect engagement with accumulating gears. These gears, however, are not associated with a winding drum but engage in pairs with a differential gearing homologous to that used in the rear-axle assembly of an automobile, except that its function is fulfilled by the use of a compact arrangement of spur gears only, obviating the use of bevel gears.

To understand the manner in which this gearing is used to effect the totalization, consider an ordinary automobile of which the speed-change gears are in neutral or the clutch disengaged, the rear wheels being jacked up. If now the right-hand rear wheel ih held stationary and the left wheel turned $m$ revolutions, the clutes shaft or "propeller" shaft will rotate through some other number, say $n$, of revolutions, depending upon the gear ratio of the car. Similarly, if the left-hand wheel is held stationary, and the right-hand wheel rotated $m$ revolutions, the clutch shaft will rotate through the same number $n$ revolutions. If, however, both rear wheels are rotated in the same direction the same number of revolutions $m$, the propeller shaft will be found to rotate through twice as many revolutions as before, namely $2n$, and this will be the case

whether the $n$ revolutions described by each of the two rear wheels takes place simultaneously, or successively, or at the same or different rotational speeds. If the right-hand wheel rotates through a different number of revolutions than the left-hand wheel, the number of revolutions of the propeller shaft will be proportional to the sum of the rotations of the two wheels, also without regard to whether or not the rotations were carried out at the same time and at the same speed.

An exactly similar sort of summation takes place in the type of leather-measuring machine now under discussion. If one traversing wheel is rotated, and the other of that pair remains stationary, no leather passing under it, the intermediate totalizing shaft $A$ rotates only half as far as it would were both members of the pair rotated by the same amount; and when the rotations are unequal in amount, the intermediate shaft $A$ rotates by an amount which is proportional to the sum or the average of the rotations of the two members of the measuring pair.

The measuring wheels are thus grouped in pairs throughout the machine, and the intermediate totalizing shafts similarly "feed" their several rotations by pairs into superior intermediate totalizing systems, until finally after several collections and averagings, the rotation is transmitted to the dial mechanism, which receives a movement proportional to the average and hence to the summated movement of all the measuring wheels.

As in other wheel machines, a ratchet and pawl are provided to prevent retrograde rotation, which in this case would be induced by the reaction effect of adjacent gear trains. In addition to the usual dial for registering the area of the individual skins, this machine provides a counter to record the number of skins measured, this being operated by the action of resetting; and an integrating dial, to show the total area of all skins measured. In the machine shown, the measuring wheels are spaced only half as far apart as in the types already described. Other things being equal, this affords, as will appear later, a considerable improvement in the accuracy of approximation to be attained in the measurement.

Some reference has been made in conversations with the author, to a type of wheel machine in which radial pins carried in the several traversing wheels are depressed by the contact of the hide and by that depression engage a suitable accumulating mechanism. So far as is known, only one such machine has been brought into this country, and information about its operating

principles and performance is very meager. It has been said however, that the particular machine imported was not successful, owing to extreme delicacy of mechanism, necessitating frequent adjustment or repair.

(*c*) SOURCES AND DETERMINATION OF ERRORS.—(*1*) *Spacing of Wheels.*—As can be easily understood without special explanation, the accuracy of approximation in the integration of an irregular area by the principles exemplified in the wheel machine is increased as the distance between the parallel measuring wheels is decreased. The practical considerations involved in the mechanical construction, such as the necessary clearance between neighboring parts and the cost of manufacture, will set a limit upon the closeness of spacing possible. The distance between centers of the rims of measuring wheels in the types of machines now commonly used; is 1½ inches.

One point of importance to be noted in connection with the errors due to insufficiently close wheel spacing is that when a tolerance of error is established upon the area measurement carried out upon the machines and a certain fraction of this error is allotted, as is requisite, to that due to the spacing of the wheels—the maximum wheel spacing permissible, to insure accuracy within this limit, can be closely calculated when a suitable outline or type of the area to be measured is determined upon and established as a standard for the purpose. H. M. Roeser, of the Bureau of Standards' staff, has given careful study to the relation of the closeness of spacing of the measuring units to the accuracy of area approximation, and is in a position to advise in detail as to the methods to be followed by the designer of a leather-measuring machine with respect to this phase of the problem. Obviously the magnitude of the error due to interval between wheels is a function of the irregularity of the outline of the hide. The more smoothly outlined the figure, the greater can be the interval between measuring wheels, for a given allowance of error, while an extremely jagged perimeter might require three or four times as many wheels per unit of machine length to permit of attaining the same degree of accuracy. Therefore, we find in this consideration, as in others to follow, a compelling reason for the adoption of a standard form of test area, a matter which fortunately raises no important practical difficulties.

(*2*) *Width of Rim.*—The next source of error is also dependent upon the shape or figure of the area measured. It will be recalled from the general discussion of this type of machine that it is the func-

tion of the measuring wheels to measure the middle ordinate of the strip which each wheel traverses. This could be done with perfect accuracy only by a wheel with an infinitely narrow contact surface or rim, and any approximation to this requirement is, of course, impracticable with present designs, because of the necessity of getting sufficient traction to drive the relatively heavy and resistant mechanism by tractive contact between the periphery of the wheel and the surface of the hide to be measured.

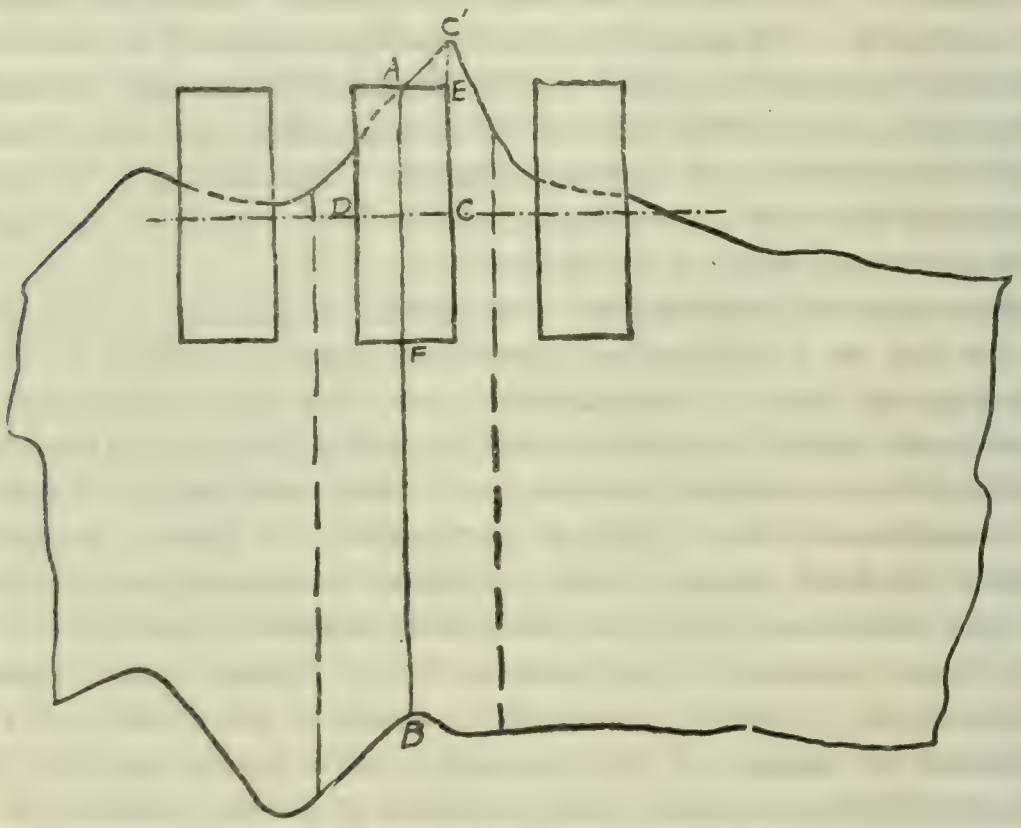


FIG. 11

Fig. 11 shows how a finite width of rim of the measuring wheel results in an exaggeration of the movement of the traversing wheels. If *AB* is the middle line of the strip which wheel *DC* is to measure, its length can be correctly measured only by a wheel which travels along the line *AB* and touches that line only. If the wheel has width, it touches a zone of which *AB* is the median, and continues to turn until every part of its tire has left contact with the hide, or in the sketch, *ADFCE* being the plan view of an exaggeratedly wide-rimmed wheel, until the point *C* of the wheel and *C′* of the hide leave contact (the thickness of the hide being neglected for the moment, this being a cause of additional delay in the completion of the traverse). Thus the ordinate of the hide is overmeasured by the amount *EC′* which represents the excess

of rotation of the wheel consequent upon the existence of driving contact outside the median line of the strip.

It will be noted that this effect, which is an important one, invariably tends toward overmeasurement, and that like the preceding type of error it is the more in evidence on irregularly or jaggedly outlined hides, since on such hides the difference between the middle ordinate of any strip and the longest ordinate within the purview of the measuring wheel is enhanced. The magnitude of this error for any given width of tire, as with the wheel spacing in the preceding section, is easily calculated, and when a limit is set upon its contribution to the total error of the machine the maximum allowable width of the wheel rim is readily established, a standard form of area again being postulated for the purposes of the investigation.

As has been suggested, this type of error indicates a very definite and desirable trend in the design of leather-measuring machines, namely, that the frictional and other resistances shall be reduced to the lowest possible value, to the end that a minimum of traction shall be required to drive the measuring disks. Reduction of the driving traction will proportionately reduce the width of wheel rim required, with a consequent improvement in the performance of the machine. There is no reason whatever to suppose that the modification here suggested will offer any serious technical difficulties, although, to be sure, it does involve to some extent the simplification of mechanical detail, as it is eminently desirable that the number of moving parts be reduced in order to make available the most potent means of obtaining the desired reduction in the driving force required. The use of high normal unit pressure between the wheels and the leather to obtain the necessary traction is, of course, out of the question, as that method would involve serious danger of marking and disfiguring the finished surface of the skin.

With regard to the matter of excessive width of traversing wheel rim, it may be noted that the author had opportunity to examine one model of a leather-measuring machine in which the traversing wheels or what corresponded to them, were constructed as a bank of rolls, filling in *all* the space available, so that the exaggeration of rim width had been carried to its highest possible limit, the width of each rim thus being equal to the center to center distance between traversing wheels. This is indicative of a number of features which would permit the user of a leather-measuring machine to obtain increased reading on hides and skins, while the

machine would still pass the usual accuracy tests applied. It will, of course, be understood that such a wide-rim machine as has been described would give accurate results on a rectangular test pattern, if this pattern were passed through normally, without being inclined to the common axis of the traversing wheels, though when passed through slantwise the excess of reading should be very apparent.

(3) *Overrun of Wheelwork.*—In all wheel machines, there will be some error due to the delay of the accumulating gear in picking up the velocity corresponding to the movement of the hide passing under it, since the wheel must be accelerated from rest by the pinion of the traversing wheel at the moment the latter has made contact with the hide. After the hide has passed out from contact, the accumulating wheel will tend to continue its rotation and will so rotate until its kinetic energy is absorbed by the frictional resistances of the mechanism and by such restoring or counterforces as are present, such as counterbalance weights, or unbalanced wheels or segments.

This error is quite large in some of the existing wheel machines, and it should be especially noted that it can not be considered as of small importance on the supposed ground that it will produce an error of constant amount in excess, and will, therefore, be cared for in the calibration of the machine. Even if the error were constant, either absolutely or relatively, at any speed, proper control of the machines would then require that a sensitive and reliable speed indicator or tachometer be part of the equipment. The only possible means for correction of this error, if it could be rectified rigorously, would be the setting of the pointer so that it would start back of the zero point, the retrograde shift of the zero being made equal in amount to the determined value of the overrun error. This is manifestly impracticable even under the best conditions, even if it were not for the fact that the error is not constant but a function of the outline or figure of the hide as well as of the number of wheels operative in a given measurement. The reason for this is clear; every time the traversing wheel pinion is lowered out of engagement with the accumulating gear, the latter spins forward a certain more or less definite amount, depending upon its previous rotational velocity, its moment of inertia, and the resistances of friction and gravity and other forces which oppose its movement. Now if the outline of the hide is such that a given accumulating gear is engaged and disengaged a second time in the traverse of the hide,

the error is doubled, approximately, due to the second opportunity of the wheel to spin ahead of its proper final position of rotation.

Experiment has shown, as will be seen on page 24, that every increase of speed of rotation will produce an increase in the readings of area obtained, and when once the contribution to the total error or variance of the machine that is deemed permissible as resulting from this cause alone, is decided upon, the correct limiting speed of operation can readily be determined by experiment. To do this, the machine will be operated with the same standard of area or with the same series of standards, beginning with a very slow speed of operation, so low that the overrun error is quite negligible, and increasing by steps to some higher speed. A curve will then be plotted with the actual speed of rotation as abscissas, and the increase of reading over the reading corresponding to the initial very slow speed as ordinates. The value of the speed of rotation corresponding to the point where this curve crosses the horizontal line defining the permissible limit of error due to overrun effect alone will be the maximum allowable rotational speed. Its determination in the manner described will present no difficulty. If there should be any doubt as to the observance by the user of this proper maximum speed, it would be quite possible to apply a speed-limiting governor so arranged as to make the machine inoperable above the predetermined speed for which it has been adjusted.

There appear to be very considerable differences between the amounts of the overrun error of the several existing types of machines, and this can be accounted for in part by the fact that in one type the accumulating gears are in balance, and their rotation is, therefore, opposed only by frictional resistances and by the counterbalance weight provided at the dial end of the mechanism to take up backlash. On the other hand, the accumulating gears of another make are not in balance but are formed as segments, so affording a considerable restoring moment to oppose the continuance of the forward rotation. In a later modification of the latter machine, the accumulating gears, while not segmental, are nevertheless designed to be somewhat out of balance, and this has a similar though perhaps an insufficient effect. This unbalance is sufficient to, and is used to return the parts of the machine to their zero position after the completion of a measurement, which it does by causing backward rotation of the accumulating gears under the action of gravity, upon the release of the system of pawls which engage these gears.

It is the opinion of the author that the overrun error is decidedly excessive on all types of existing wheel machines, even when these machines are run at the lowest speeds now in commercial use, and there is little doubt that, in some instances, wheel machines have been deliberately overspeeded to produce overmeasurement. At least one instance has been reported of a wheel machine being regularly run at 100 per cent above its rated operating speed, a procedure which must unavoidably produce enormous errors due to overrun.

Definite numerical results on the overrun error are given in the table below, the first three machines being wheel machines—two of one make and one of another—and the last two machines being pin machines. The second column under A is significant in that it clearly bears out the statements made above in the present section, that the overrun errors are increased by a manner of use of the machine which permits the accumulating gears to be engaged and disengaged more than once in the traverse of a single skin. It will be seen that the values in column 2 for machine A are very definitely higher than those in column 1. It will be understood that in passing the skin through the machine with its long axis perpendicular to the axis of the feed roll, the wheels at the limits of the area to be measured will naturally be lifted and lowered a number of times on account of the serrated nature of these two corresponding portions of the hide perimeter.

**TABLE 2.—Readings on Skin No. 6**

[Test No. 20725. All readings of area in square feet]

| | Actual area of skin No. 6 (planimeter) | Readings on machines designated as— | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | A | | | B | | | C | D | E |
| | | Condition 1[a] Speed normal | Condition 2[b] Speed normal | Condition 1[a] Speed 12 r. p. m. | Speed 64 r. p. m. | Speed 30–60 r. p. m. | Speed 18 r. p. m. | Speed normal | | |
| | 8.74 | 8.70 | 9.00 | 8.65 | 8.80 | 8.62 | 8.50 | 8.75 | 9.00 | 8.70 |
| | ..... | 8.85 | 8.90 | 8.65 | 8.75 | 8.62 | 8.50 | 8.62 | 8.95 | 8.80 |
| | ..... | 8.80 | 8.88 | 8.62 | 8.75 | 8.75 | 8.62 | 8.65 | 9.00 | 8.70 |
| | ..... | 8.88 | 9.00 | 8.62 | 8.63 | 8.75 | 8.50 | 8.75 | 8.90 | 8.90 |
| | ..... | 8.95 | 8.85 | ..... | 8.82 | 8.75 | 8.52 | ..... | 8.90 | 8.75 |
| | ..... | 8.85 | 8.90 | ..... | 8.75 | 8.50 | 8.64 | ..... | ..... | ..... |
| | ..... | 8.90 | 8.80 | ..... | 8.75 | 8.60 | 8.62 | ..... | ..... | ..... |
| | ..... | 8.75 | 9.00 | ..... | 8.75 | 8.58 | 8.60 | ..... | ..... | ..... |
| | ..... | 8.90 | 9.03 | ..... | 8.75 | 8.62 | 8.50 | ..... | ..... | ..... |
| | ..... | 8.90 | 8.90 | ..... | 8.75 | 8.55 | 8.60 | ..... | ..... | ..... |
| Average | 8.74 | 8.85 | 8.93 | 8.64 | 8.75 | 8.63 | 8.56 | 8.69 | 8.95 | 8.77 |
| Error of machine | ..... | +.11 | +.18 | −.10 | +.01 | −.11 | −.18 | −.05 | +.21 | +.03 |
| Per cent error | ..... | +1.3 | +2.2 | −1.1 | +.1 | −1.3 | −2.1 | −.6 | +2.4 | +.3 |

[a] Long axis of skin parallel to axis of feed roll.
[b] Long axis of skin perpendicular to axis of feed roll.

It was noted that the error due to overrun tends to be greater (absolutely, if not relatively) the larger the skin measured. In the case of one series of measurements made with a large skin on machine *A*, the following results were obtained:

| | | |
|---|---|---|
| Reading of area at 14 r. p. m. | square feet | 22.33 |
| Reading of area at 59 r. p. m. | do | 23.21 |
| Difference | do | +.88 |
| Difference in per cent | | +3.9 |

Readings were also taken with the same machine using a rectangular sheet of leather, the area of which was determined by measurement and calculation to be 9.86 square feet. The mean of 20 readings on this machine was 10.08 square feet, the error thus being 2.2 per cent in excess at normal running speed, even for a rectangular outline, which, as has been shown, rather favors a low value of this particular error.

Additional data on this question are available in Table 1, in which it will be seen that each of the power-driven machines shows a decided change in reading when its speed is reduced from that at which it has been regularly run to a very low speed; this, of course, being proof direct that the wheel machines considered have all been run at a speed higher than is proper. The following brief analysis will show the amount of this difference:

| Machine | Errors and differences in per cent of true area | | |
|---|---|---|---|
| | At normal speed of operation. Average error | At slow speed of operation. Average error | Difference |
| A | +4.4 | −0.7 | 5.1 |
| B | + .5 | − .2 | .7 |
| C | + .8 | − .9 | 1.7 |

It is well to emphasize the fact that this fault can not, as has been assumed by manufacturers, be corrected in any given machine by running it at that speed which would result in a zero error in a particular skin (or test sheet), since the effect is, as has been shown, dependent upon the outline or figure of the skin, and the apparent zero error so obtained could not possibly be reproduced in succeeding measurements on other skins. As has been stated, the only remedy is to determine for each type of machine that speed at which the error due to overrun becomes equal to the partial or constituent tolerance allowable for that error.

In the absence of more exact information regarding the moments of inertia and opposing resistances of the accumulating gears of the wheel machines, the speed rating of such machines should be based not upon the number of revolutions per minute of the feed roll, as has been common, but upon the circumferential speed of that roll, thus affording a comparison of the rates of translation or traverse of the hide or skin to be measured, which is, of course, the fundamental and useful basis for comparison of operating speeds.

The author can not but believe that the emphasis placed upon speed of operation of these instruments is decidedly a fallacious one. It is his opinion that the cost of measurement, in so far as it appears in the cost of labor of the measuring machine tender, per square foot of area measured, is a factor of much less importance than the cost of inaccurate and variable measurements, or differently expressed, the cost to a tanner or shoe manufacturer of seriously deficient or excessive measurement, such as there is every reason to believe existing machines will customarily and regularly give, may be so great that the speed of performing the measurement practically drops out of consideration. It might even be economical, in the case of valuable leather, to carry out the measurements by the use of a planimeter, when it is considered that the difference between successive readings on the same machine may amount to more than 4 per cent (see Table 4), which in the case of a single skin of 15 square feet area, might amount to a money loss of nearly a dollar. When it is considered that this measurement is performed in a few seconds, it appears absurd to emphasize labor cost and to ignore the cost of machine error. Even at the present high prices for labor, a great many skins can be measured for $1, even by the most slow, painstaking, and accurate method available. The writer, whose viewpoint, to be sure, is that of one outside the leather industry, and who may, therefore, be inadvertently ignoring some essential facts or difficulties inherent in the situation, is convinced that the emphasis which has been placed upon the speed of measurement (at the cost of accuracy) is essentially a false one, and that steps should be taken to study the economics of this situation from an engineering point of view, in order to determine with assurance, to what extent slowing up of the process, if it result in enhanced accuracy of measurement, will be economical. This problem is a perfectly definite and determinate one and the studies which it will require can be conducted at very small expenditure of time and effort. It will then be possible to give proper weight to the

opposing factors of speed and accuracy, which now seem to be antagonistic.

One expedient, which may already have been proposed, by which the overrun errors can be very largely eliminated, would be the use of a brake or dog so arranged as to come into operation the instant the traversing wheel has dropped back into contact with the feed roll. Within certain limits, of course, a brake of constant application, having for its purpose simply to increase the torque required to rotate the accumulating gears, would be of service. It would be necessary that it should not increase the energy required to operate the machine sufficiently so as to make slipping between the traversing wheels and the skin imminent or, collaterally, to require a widening of the rims or increase of the contact pressure of the traversing wheels. There is some doubt whether practically the application of the braking arrangement would pay, since unless constantly in operation it would unavoidably add complication to the mechanism, a result which might be sufficiently detrimental to offset the relatively small advantage to be gained. All consideration of this question by the author has seemed inescapably to lead to the one conclusion, namely, that the only effectual expedient, if wheel machines are used, is to lower the speed of traverse to the required value, however low an operating speed that may involve. Thus, if the manufacturer is required to specify the speed of operation of his machine in feet per minute of passage of leather, that speed being sufficiently low that the partial tolerance to be established upon this error will not be exceeded, then the buyer of the machine may make his decisions, drawing a proper balance between the speed of operation and the other at least equally important factors involved.

In conclusion, with respect to the three types of error just discussed, it will be seen that the wheel machines show a very definite dependence upon the outline or figure of the hide measured, or in other words, that two hides of identical area but differing outline would be differently measured by such a measuring machine, the greater reading being obtained in the case of the hide of the more irregular outline. The first two causes produce an error which is increased by increasing acuity of the angle which a part of the outline of hide makes with the plane of the corresponding measuring wheel, while the third cause is dependent upon the jaggedness of the outline in the sense that the error is increased by interruption of the hide surface by a reentrant angle of such character that the contact of the hide with a given wheel ceases for a space and is

then resumed. If the hide has cut-in portions, the normals of which lie in a general direction perpendicular to the direction of the motion of the hide through the machine, the sort of action referred to will take place, in which one or more wheels are lowered out of engagement with the accumulating gears, and then later lifted so that the accumulating movement is reinitiated.

(4) *Effect of Thickness of Material.*—On most of the wheel machines in use, an error exists due to the variation of the thickness of the material being measured, which arises in this way: Assume that the traversing wheels and the feed roll are running in contact and that the pinion of the traversing wheel just fails of engagement with the corresponding accumulating gear; now, if an extremely thin piece of material, such as tissue paper, be entered into the machine, the traversing gear will be lifted at the moment the advancing edge of the sheet reaches the line connecting the center of the feed roll and the center of the traversing gear. The accumulating gear will at once start to rotate (assuming that the fit and alignment of parts of the machine under consideration are ideal, so that its accumulating gears can be engaged by an extremely small rise of the corresponding pinions). When the piece of thin material has entirely traversed the traversing wheel, it will pass out of contact with that wheel and permit it to be lowered from engagement with the remaining gears just at the instant at which the retreating edge of the sheet leaves the lines of centers of the traversing wheel and the feed roll.

Now, consider the case of a thick sheet of material, say a heavy hide of leather. The traversing wheel and the feed roll will begin to separate at the instant the sheet of material makes contact with both of them (see Fig. 12), which will occur before the advancing edge of the thick sheet reaches the line connecting the centers of the measuring wheel and the feed roll. The accumulating gear will therefore be engaged and begin to rotate as soon as the first contact and consequent lift of the traversing wheel by the sheet has occurred, and as the sheet emerges after having passed under the traversing wheel that wheel will continue to turn and the accumulating wheel will continue its engagement until the retreating edge of the sheet has passed some distance beyond the line of centers and out of contact with the feed roll and the traversing wheel. The effect of this action is that the traversing wheel will have turned through an angle which is greater than the length of the middle line of the strip which it is the function of the traversing wheel to measure, and the readings of the machine will be in excess

by an amount equal to the sum of the excess rotations which have been contributed by each of the traversing wheels engaged in the measurement. It will be seen that the magnitude of this effect for each traversing wheel is a function of the diameters of the measuring wheel and the feed roll, of the engagement clearance between the traversing wheel pinion and the accumulating gear, and of the thickness of the hide, the error being greater for thicker hides.

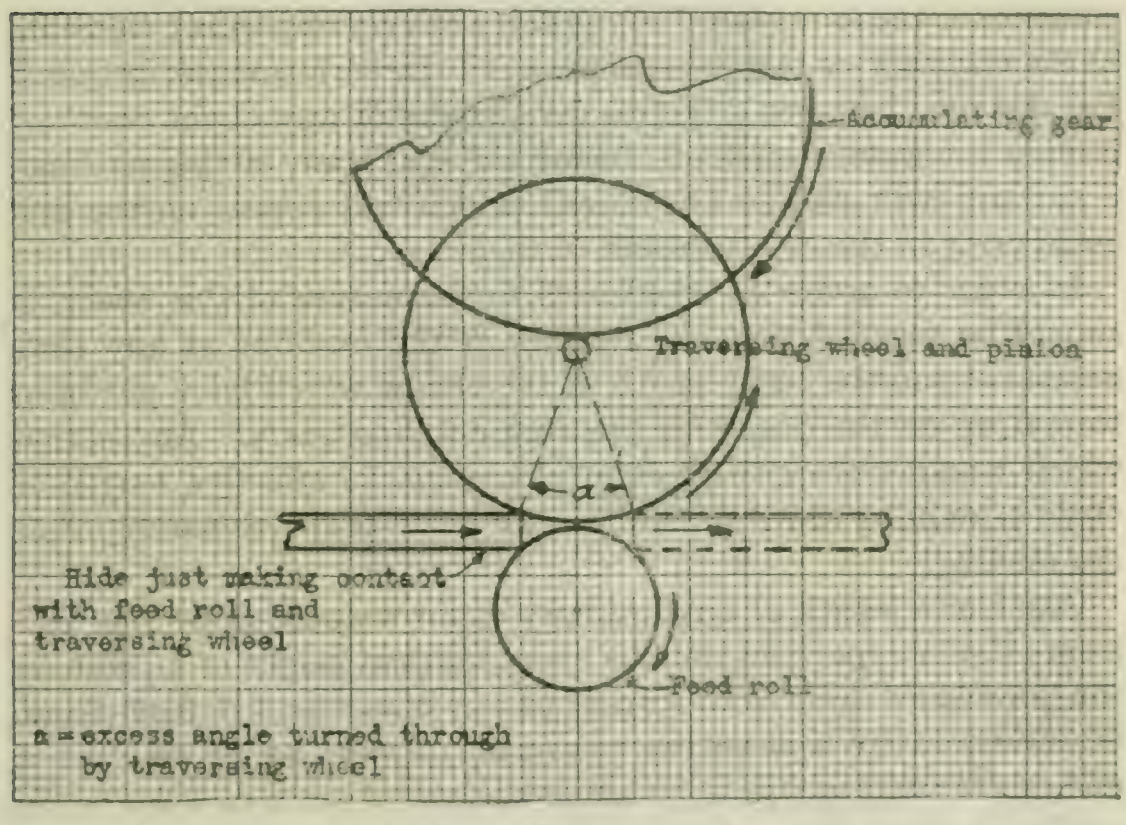
Accumulating gear
Traversing wheel and pinion
a
Hide just making contact with feed roll and traversing wheel
Feed roll
a = excess angle turned through by traversing wheel

FIG 12

The only method known to the author which will accurately and satisfactorily compensate for this error is to provide a means of lowering the feed roll so that the clearance between the pinions of the traversing wheels and the accumulating gears is made equal to the average edge thickness of the hides being measured at any one period. A graduated lowering device, so arranged that it could be operated to set an indicator at a reading to correspond to the measured thickness of the hide as determined by a suitable thickness gage would seem to serve the purpose. It is believed that some such arrangement as this is to be found on one of the foreign-made types of leather-measuring machines, of which only a few examples are in this country.

It is of course to be understood that the compensation obtained in this way can not be a perfect one on account of variations in thickness from hide to hide, and in fact in different parts of the same hide. It does not seem, moreover, that any machine using wheel contacts as its operating principle can provide complete compensation.

(5) *Variance Due to Imperfections of the Linkwork.*—The chains which operate to translate the motion of the measuring gears into rotation of the index hand at the dial are very important elements in the accuracy or rather consistency of the performance, in that if the distance between any two given links of any chain does not remain accurately constant during the operation of the machine, a variant error will be introduced, which will appear on the dial as an error in the measurement of the area.

In order to arrive at an idea as to the nature of this effect, it should be recalled that the reading of the machine at any time depends upon the total length of the chains which have not been wound up on the drums of the accumulating gears. Any action which would have the effect of changing the effective length of chain remaining unwound would, of course, proportionately affect the reading.

Consider a length of any ordinary chain suspended by one end from a rigid support, and let the exact vertical height of a point on the lowermost link, with respect to any convenient datum plane, be measured by a sensitive measuring device, as by sighting a micrometer microscope upon a fine horizontal mark or a dot or tip applied to that link. Let the height of this mark be observed and recorded. Now, it is obvious that if the chain be simply shaken, or bent or swung, and again allowed to come to rest in the vertical, the height of the reference mark will have changed, due to more or less irregular changes in the contact relationships of the several links as seen in the sketch (Fig. 13). This change in the effective length of the chain is a secondary result of the friction between the links, and produces what is termed "variance" in the indications of any instrument of whose mechanism it forms a part.[3] All types of chains are subject to this error, although, of course, its amount will vary with the type and dimensions of the particular chain under consideration. Even cords, which were once used as connectors in leather-measuring machines, show a very similar effect, due to the internal friction or elastic hysteresis

[3] See p. [illegible] of B. S. Scientific Paper 328, "Variance of Measuring Instruments," by the present author.

in the fibers and strands. Another source of variance due to chain action, having a similar effect, will originate at the points where the chain makes contact with the pulleys and drums around which it wraps, as the result of a certain latitude in the disposition

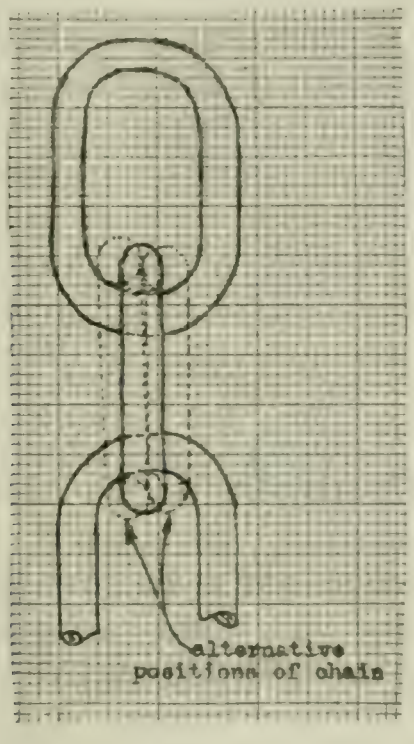


FIG. 13

of the chain laterally as it enters into contact with the pulley groove as shown in Fig. 14. This lateral variation in position has the effect of slightly altering the effective or net length of the chain with respect to its contribution to the indication at the dial.

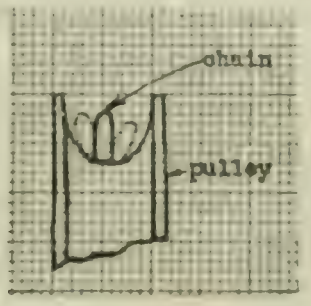


FIG. 14

The most invariant type of flexible connector available is an easily flexed, slender, flat (metallic) tape or wire, the internal friction of which will be very low, and the length of which will be correspondingly invariable. This type of connector should serve excellently for the purpose.

If a chain is used, a type should be chosen which is as little as possible subject to variability in the distance from link to link. While the individual variations from link to link may be very small in amount, nevertheless in the total length of chain involved in the numerous separate elements of a leather-measuring machine, these variations may at times sum up to a large value when reduced at the dial to an equivalent of area, as every link of every chain is liable to suffer a change in its contact relationships and so occasion a change in the effective length of the connections throughout. One machine examined uses a rather favorable type of chain, in that it is almost perfectly circular in cross section, and has a smooth, regular surface, both of which properties assure, in so far as possible, the uniform engagement of the chain with the pulleys over which it passes. This is a factor which, as has been shown, is also important in obtaining constancy of reading.

Another source of variability in the mechanism of the wheel types of leather-measuring machines is the complexity and multiplicity of connections and contacts in the linkwork generally. It is to be recalled that, in a 5-foot length machine of a common make (this being the usual working length), there are 11 pin or hinge joints in each of 5 lever systems, or a total of 55 operating joints in the averaging levers alone. In addition there are an enormous number of separate turning pairs consisting of link contacts comprised in the 40 chains involved, 40 separate bearing units supporting the accumulating gear journals, making 80 individual bearing elements, besides a small number of joints in the dial mechanism.

The importance of this variance inherent in the operation of a complicated mechanism can be judged when it is considered that, in the case of a rectangular leather sheet of 9.86 square feet area, an extreme variation or "spread" amounting to 5.1 per cent was observed in a series of 20 consecutive readings. These readings ranged between the wide limits of 9.85 and 10.35 square feet and this large value was practically duplicated in 2 sets of readings in the 20 referred to. Probably most of this variance is chargeable to the unavoidable mechanical imperfections of the mechanism or link-work, since the rectangular sheet favors maximum constancy of overrun error and a minimum variance due to the width of wheel rims, although, to be sure, under exceptional conditions the rectangular sheet might favor a high value of that portion of the variability having its source in excessively wide spacing of traversing wheels.

No instrument maker would expect such a mechanism to give satisfactorily reproducible results. In other mechanical measuring instruments, whenever high complexity of mechanism is unavoidable in carrying out the function prescribed, the utmost refinement in bearing and connector elements is provided for, when accurate results are desired—as by the use of ball bearings or conical pivots, by extremely careful fitting of parts with respect to bearing clearances, by substitution of tapes and similar flexible connectors for chains and links, etc. The necessity for modification of existing designs in these essential respects can be judged by reference to a later section, Variance, under the general heading "Determination of Machine Performance."

Another source of variance arising in the elements of the mechanism is that due to the ratchet and pawl action used in preventing reverse rotation of the accumulating gears until they are reset to the zero position. It is clear that, with teeth of finite spacing, some retrograde motion will take place before the locking position is attained. This motion is subject to the laws of chance, and the error produced is equally likely to be positive or negative so that no persistent error results, but only another manifestation of variance, that ever-present enemy of accuracy.

On one of the common leather-measuring machines there are about 550 teeth on each of the accumulating gears which serve as ratchets. As only a partial rotation of each of these wheels occurs in the traverse of a skin, it is seen that the proportionate variance due to tooth spacing is by no means negligible.

Possible expedients for reducing this error are to use (1) finer (more closely spaced) ratchet teeth, (2) "stepped" or offset multiple pawls with the existing tooth spacing, (3) the so-called toothless ratchet or clamping ratchet.[4]

The last expedient does not totally eliminate the retrograde rotation, as might be supposed, since a certain small reverse movement is required before the locking becomes operative.

The variance due to ratchet-tooth spacing, like that due to spacing of traversing wheels and the width of wheel rim, can be definitely calculated, from a knowledge of the tooth spacing and the equivalent of rotation of each accumulating gear in terms of area at the registering dial. The range of variance due to this cause, like that due to the others discussed, should be determined

[4] References on damping ratchets: Mechanics of Engineering and Machinery, Weisbach (Klein's translation, 1896) 8, Pt. I, Sec. II, pp. 871–875; The Constructor, Reuleaux (Supplee's translation, 1904) pp. 158–162; Principles of Mechanism, Robinson, 1876, p. 296.

in advance, and restricted within a predetermined partial tolerance of error established as the maximum permissible limit of the magnitude of this effect alone.

*Recapitulation: Persistent Positive Errors.*—A significant fact in relation to three of the sources of error detailed above, namely, that of excessive width of traversing wheel rims; that of overrun of the traversing wheels; and that of the thickness of the material being measured; is that each tends to increase the readings above the true area, while the other two major sources of error (excessive spacing of traversing wheels and imperfections of the linkwork) are probably as likely to result in deficient as in excess measurement. On the whole, then, it may be said that any machine having any or all of the three faults in the first group named will tend to measure in excess. Any characteristic tendency of a commercial measuring device to give readings regularly in error in the same direction is to be sedulously restrained, and it is impossible to overemphasize the need for especial attention and study in the design of this apparatus, in order to eliminate wherever possible (and it usually is possible, though radical redesign may be necessitated) all individual sources of error having a persistent and positive tendency to introduce errors of a particular sign.

This whole question of increased precision in the measurement of leather, which seems imperative in the light of the data of this investigation (as well as of those of the British investigation reported by the National Physical Laboratory) seems to the author so important that he would again emphasize the disparity between the precision attained in the measurement of leather and that in the measurement of other commodities of similar or less value. The average price of copper per pound is about one-half that of leather per square foot, yet no smelter or dealer would consider using, for purposes of purchase or sale, a weighing scale having the enormous inaccuracy or variability which is characteristic of the usual leather-measuring machines. In weighing scales, instead of allowing a plus or minus variation of from 1 to 3 per cent, as has been tolerated in the case of leather-measuring machines, the variation and error combined are restricted to $\pm 0.2$ per cent or less, depending upon the type. For a weighing scale used indoors, $\pm 0.1$ per cent is the combined allowance for error and variation, after the scale has seen service. The tolerance on a new scale used indoors, is set at one-half of this value, under the assumption that a smaller tolerance should be

established on new apparatus to permit of the service tolerance being maintained for a reasonable period after the apparatus has been put into use.

(*6*) *Secular Changes in Hides and Skins.*—The question of accurate measurement of hides and skins is complicated by the fact that the dimensions of these materials are far from permanent, in that they suffer considerable change in each direction from variations in temperature and humidity. The time available did not suffice for an analytical study of this change, but on one set of six typical calfskins received from a Massachusetts tannery, the changes in area from the time of the receipt of the skins at the Bureau was considerable, ranging in amount for the several skins from 1 to 2½ per cent approximately, in a period of 37 days.

It is by no means certain that these changes are reversible ones. It is quite probable, in fact, that a portion, at least, of the changes shown is due to a secular transformation which takes place in the material subsequent to the manufacturing process. The nature and character of this change will probably be more significant to leather technologists, and is here dismissed without further conjecture as to its causes and the degree of its dependence upon the processes of manufacture.

## III. METHODS OF TESTING LEATHER-MEASURING MACHINES

### 1. FORM AND MATERIAL OF THE AREA STANDARD

Field calibration of leather-measuring machines requires the use of standards of area. The primary requisites for such standards are the following: (*a*) Thickness sufficient to raise into operation the traversing wheels of the usual types of leather-measuring machines; (*b*) A surface offering a reasonable tractive resistance, so as to drive the traversing wheels without appreciable slip; (*c*) An outline typical, in so far as may be, of the outline of the hides and skins usually measured; (*d*) High permanence of dimensions under (1) changes in temperature; (2) changes in humidity; (3) the distortion due to the stresses incident to use; (*e*) Durability or resistance to mechanical wear.

The first of these requires the use of a material comparable in thickness to ordinary upper leather, say 0.06 inch (1.5 mm) or more. The second requirement is fulfilled by any flexible material similar to leather or cloth having a surface giving a reasonable friction against the metals. This requirement eliminates materials like the pyroxylin plastics, such as celluloid, and very thin

sheet metals, other properties of which might seem well suited to the work.

Sheets of leather, as has been shown in the foregoing section, are far from permanent in their dimensions. Leather is decidedly affected by variations in humidity, and doubtless, also, to a large degree by variations in temperature. In addition it is to be expected that the deformations to which a sheet is subjected in the testing of leather-measuring machines would alter its dimensions gradually were it made of a material having the low elastic constants and relative "plasticity" of leather.

In seeking for materials which should give promise of the best properties for this use, the following were suggested, but time has not been available to determine their physical constants in order to make certain their adaptability for this purpose. In order of their probable serviceability these two should be given consideration:

1. A pyroxylin-coated textile material of the type now much used in the manufacture of artificial leather. Rough measurements made upon a small sample of this material indicated fair permanence under changes in humidity. It is to be expected that its thermal expansivity would be high, like that of many other organic substances. A question still to be investigated in materials of this sort is the obtaining of the necessary thickness. This should offer no difficulty if the manufacturer of artificial leather does not object to coating a special, heavy fabric.

2. Rubber or composition sheet packing containing an inserted wire fabric. Material of this character, using a brass-wire fabric, is already on the market as a high-pressure steam packing.

This material can be produced in almost any desired thickness, is reasonably flexible, and should be quite durable in use.

The determination of the essential properties of either of the two materials suggested above will be a simple matter; the coefficients of expansion under varying humidity and varying temperature are easily and quickly measured.

With regard to the form of the test sheet, careful experiments have shown that the outline of the area measured affects the reading of the machine, this arising, as has already been explained, from the effects of overrun in the mechanism, the width of traversing wheel rims, and the spacing of the wheels. On this account it will not be satisfactory to test leather-measuring machines with sheets of rectangular or circular outline as was customary up to the time of the Bureau's investigation. With areas of such outline

but a single engagement and a single disengagement of any given traversing wheel will take place, whereas with the ordinary skin twice as many engagements and disengagements of some wheels may occur. Moreover, a right-line perimeter does not develop the variance due to excessive width of wheel rim and to excessively large interval between wheels. That this is the case, will, of course, be quite clear from the paragraph above, concluding the discussion of the first three types of error of the wheel machines. The results of the analytical investigation of the performance of leather-measuring machines described in the first section of this paper showed clearly that the use of rectangular test sheets was resulting in the certification or acceptance by weights and measures authorities and by the manufacturers, of machines which were affording apparently satisfactory results when used with such standards of area, but which, as it developed, were subject to very large and intolerable errors when used on the irregularly outlined figures of the actual hides and skins.

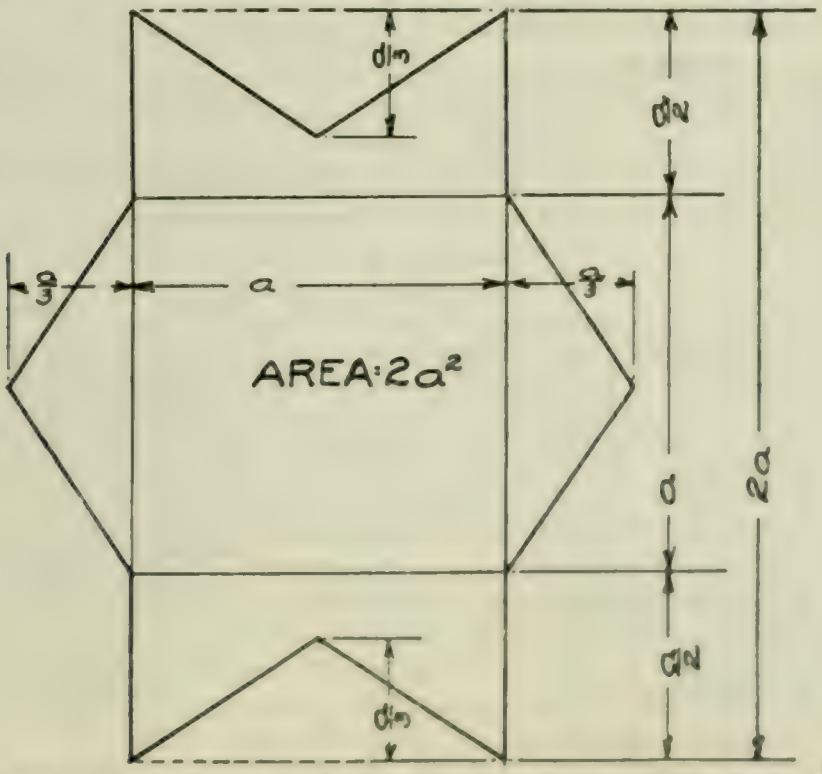


FIG. 15.—*Original form of area standard developed at Bureau of Standards, later replaced by the type shown in Fig. 16*

As a result of these deficiencies of the usual type of test sheets, an attempt was made to design an outline which would afford a rough approximation to the figure of a hide or skin, and which should, at the same time, be easy to prepare and to calibrate. With this in view, the outline defined in Fig. 15 was designed,

but since that time Max Sasuly of the Bureau of Standards has suggested and laid out an outline of improved form. This, shown in Fig. 16, is equally easy to prepare, while on account of its more ob-

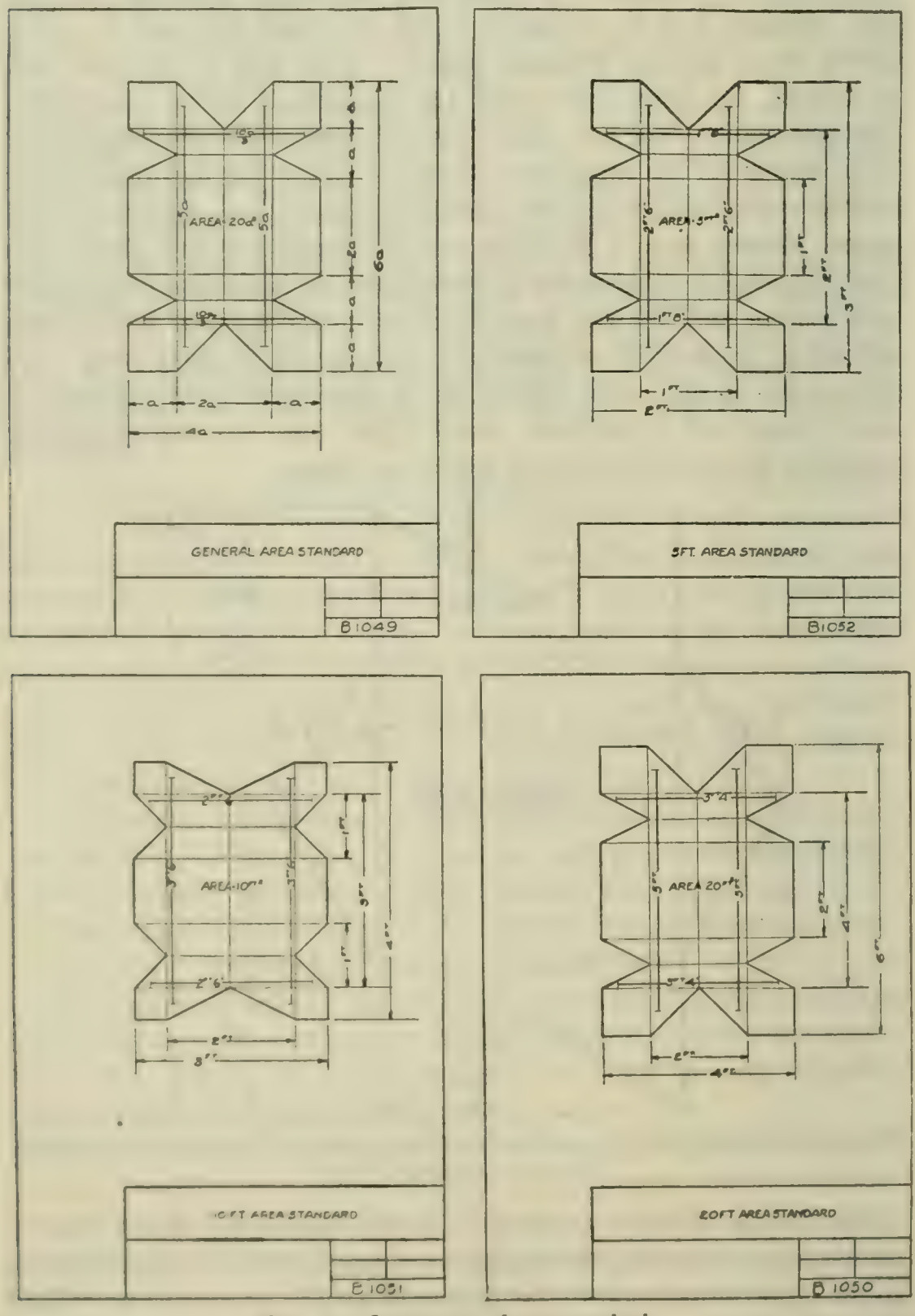


FIG. 16.—*Latest type of area standard*

As compared with that shown in Fig. 15, this has the advantages of greater durability, more effective outline characteristics, and greater ease of preparation. The first figure given is a general or type standard in which the dimensions are given algebraically; the other three are calculated for specific areas of 5, 10, and 20 square feet, respectively.

tuse angles and rectangular boundary, it is less likely to become frayed in service, and will be more readily guided through the measuring machine. It will be noted that while the outline affords the desired irregularity, the area is, nevertheless, a very simple function of its leading dimensions. The following is excerpted from the discussion which was sent out by the Bureau, accompanying blue prints defining these new standards of area, at the time the information regarding them was given to the leather trade (December, 1917):

With reference to the question of standard patterns for testing leather-measuring machines, we would say that since our previous correspondence with you, we have developed another style of pattern which has certain advantages over the star-shaped pattern originally recommended (our report to the Massachusetts Commissioner of Weights and Measures, under date of Feb. 5, 1917). Blue prints showing the relative dimensions of this new design, and showing the particular dimensions for suitable 5, 10, and 20 square foot areas, are inclosed. One advantage of this style is that there are no projecting acute-angled corners that are liable to be bent in handling. Second, the patterns can be made from paper of common integral sizes, 2, 3, and 4 foot widths, which is more readily obtainable and has its edges cut parallel. Third, the dimensions are nearly all integral values, so that the laying off of the pattern involves no difficult measurements nor the use of special scales.

You will note by the shape of the design that the pattern is most readily cut by laying off on the rectangular sheet of paper of the required size, parallel lines at distances *a* and *2a* from each end, where *a* is one-sixth of the total length or one-fourth of the width; also two lines parallel to the sides at a distance *a* from the sides. The intersections of these lines with the edges then serve as the points from which six triangles are cut out of the rectangular piece of paper, the apices of these triangles being at equal distances from the edge of the paper in each case. It is not necessary for correctness of area, though it is for the sake of uniformity of outline, that these triangles be isosceles—(that is, that they have two sides and two angles equal) provided the sides meet in the lines at the distance *a* from the edge of the paper. The area of each triangle will be its base (either *a* or *2a*) times one-half the height ($\frac{1}{2}a$).

In the suggested form for a 10-square foot area inclosed, the general form is varied slightly in order to use integral foot dimensions for the rectangular sheet of paper, making use of a 3-foot width of paper, and to use integral lengths for the bases of the triangles (1 and 2 feet), while the heights of the triangles are in each case 6 inches. Another feature of this design is the drawing on the pattern of four lines which may be called normal or control lines, inasmuch as they are used as a means of checking or proving the area of the pattern. Two of these lines extend lengthwise of the pattern, parallel to each other, and should have a length of about five-sixths of the length of the pattern. The other two extend across the pattern and should have a length of about ten-thirds of *a*. The lengths for these lines are shown in the illustrations. They should be measured at the same time as the other dimensions of the pattern are measured, and after the pattern has been cut the measurements should be marked on the pattern in each case. The exact area of the pattern as computed from measurements made at the same time should also be marked plainly on the pattern. Then, occasionally, in future use of the pattern, the control lines should be measured, preferably with a steel tape graduated to tenths of inches. The amounts by which these measured lengths differ from those shown on the pattern should be averaged for the longitudinal lines and for the transverse lines separately, and the percentage which

these amounts are of the total lengths of these two sets of lines respectively should be computed. These two percentages when added together algebraically will be the percentage by which the area of the pattern, under the conditions at that time, differs from the area marked on the pattern.

For example, suppose in the case of the 20 square foot area, the lengths of the longitudinal lines drawn on the pattern were 60.02 and 60.05 inches, respectively, at the time the pattern was made, while those of the transverse lines were 40.01 inches and 40.07 inches, respectively, and that the then calculated area of the pattern is 20.01 square feet. If, at some later use of the pattern, the lengths of the first two lines are 60.12 inches and 60.13 inches, the changes in these two lines will be 0.10 inches and 0.08 inches, respectively; giving an average increase of 0.09 inches, or 0.15 per cent. Likewise, suppose that the measured lengths of the transverse lines at this time are 40.16 inches and 40.24 inches. The changes in these lines will then be 0.15 inches and 0.17 inches, an increase of 0.16 inches or 0.4 per cent. All of these changes are increases; hence, adding together 0.15 per cent and 0.4 per cent, we have 0.55 per cent as the change in area of the pattern. In other words, the pattern will be 0.11 square feet larger under these conditions than when it was standardized; that is, its area when in use at the time of the later measurements above detailed will be 20.12 square feet.

It is desirable to have these pairs of base lines at right angles to each other as the expansion and contraction of paper with changes in humidity are different in the two directions of the sheet. Two lines in each direction are suggested, as an average of two will give more accurate results. It may be found, however, that the measurement of one line in each direction will be sufficient for most purposes. In such cases, however, the percentage change of each line should be computed in the same way and the results added together to give the percentage change in area.

For the original measurement of the pattern, it is suggested either that the parallel lines at distances $a$ and $2a$ from the ends and sides be drawn carefully, that is, as straight and as parallel to the edges as possible, and that the distance of these lines from the edge of the paper at each side of each triangle be measured with a steel rule or tape and the mean of each pair of such measurements be used as the height of the triangle in question, provided, of course, that the triangle has been so cut that the apex lies in the line at distance $a$ from the edge of the paper; or a straightedge may be laid in coincidence with the edge of the paper on each side of the corners of the triangle and the height of the triangle measured by means of a steel square laid against this straightedge and passing through the apex. The length and width of the sheet should, of course, be measured at both ends and sides, and the average taken in each case, and the bases of the triangles should be measured along the edge of the paper. The total area can then be found by subtracting from the rectangle of the sheet the sum of the areas of the six triangles as obtained by multiplying their bases by one-half their heights. A suggested form of computation is appended, with sample dimensions inserted to show the method of calculation used.

**TABLE 3.—Sample Form of Computation of Areas of Patterns for Testing Leather-Measuring Machines**

| | First measurement: left side, inches | Second measurement: right side, inches | Mean area | |
|---|---|---|---|---|
| | | | Inches | Square inches |
| Length of rectangle | 72.06 | 72.02 | 72.04 | ..... |
| Width of rectangle | 47.98 | 48.02 | 48.00 | ..... |
| Area of rectangle | ..... | ..... | ..... | 3,457.92 |
| Base triangle A | 24.01 | ..... | ..... | ..... |
| One-half base triangle A | 12.005 | ..... | ..... | ..... |
| Height triangle A | 11.99 | 12.01 | 12.00 | 144.06 |
| Base, triangle B | 12.00 | ..... | ..... | ..... |
| One-half base, triangle B | 6.00 | ..... | ..... | ..... |
| Height, triangle B | 11.98 | 12.04 | 12.01 | 72.06 |
| Base, triangle C | 11.98 | ..... | ..... | ..... |
| One-half base, triangle C | 5.99 | ..... | ..... | ..... |
| Height, triangle C | 12.00 | 12.02 | 12.01 | 71.94 |
| Base, triangle D | 24.00 | ..... | ..... | ..... |
| One-half base, triangle D | 12.00 | ..... | ..... | ..... |
| Height, triangle D | 12.00 | 12.01 | 12.005 | 144.06 |
| Base, triangle E | 12.04 | ..... | ..... | ..... |
| One-half base, triangle E | 6.02 | ..... | ..... | ..... |
| Height, triangle E | 11.98 | 12.02 | 12.00 | 72.24 |
| Base, triangle F | 12.00 | ..... | ..... | ..... |
| One-half base, triangle F | 6.00 | ..... | ..... | ..... |
| Height, triangle F | 12.00 | 12.02 | 12.01 | 72.06 |
| Total area of six triangles | ..... | ..... | ..... | 576.42 |

Area of pattern=3467.92—576.42=2881.50 square inches=20.01 square feet.

A set of three test sheets of 5, 10, and 20 square feet area, respectively, and possibly one of 30 square feet, should be provided for the regular use of the inspector of leather-measuring machines. For the larger machines occasionally found, suitable sheets up to the 60 square feet capacity will have to be provided. It does not appear that the use of several sheets in succession, in order to obtain a calibration of the upper range of capacity, can at present be considered satisfactory, as the effect on certain of the machine errors, as involved in the traverse of a succession of separate sheets, has not been investigated. It might be suggested that a standard of area should be designed such that its perimeter would fit into that of another standard, so that two or more such standards could be passed through the measuring machine in such a way as to form a practically continuous sheet. It does not appear, however, that this is a practicable solution at the present time, and the best expedient seems to be the use of an adequate number of standards to obtain by their use singly, a calibration of the machine over its full range of graduation.

The sheets, when rolled up, may be carried in cylindrical fiberboard or metal tubes, which will serve to protect them from the weather and the rough handling incident to transportation.

### 2. DETERMINATION OF MACHINE PERFORMANCE

In any measuring instrument, accuracy, or accordance of the indication with the true value of the quantity measured, can be manifested in either one of two ways. (True or perfect accuracy in any measurement does not, of course, exist, and only a relatively high, or substantial exactness is implied in the present use of the term.)

1. An invariable and consistently reproducible correctness of indication on all successive determinations made at every value of the quantity being measured. This may be termed "invariant accuracy."

(2) Errors of varying magnitude and sign, which appear as deviations about the true value of the quantity being measured, such errors having, however, a mean value which, when a large number of observations are taken, becomes equal to zero. Performance of this sort may be termed "group" or "statistical" accuracy.

Unfortunately, the above distinctions have not in the past been used as the basis of discussions of measuring instrument performance, and much confusion has resulted. Instruments have been treated as simply inaccurate when in point of fact they were highly variant. The high variance may easily be of far greater importance than a high invariant inaccuracy, as it is clear that almost any instrument can be corrected, either by adjustment of its mechanism, or by suitable regraduation of its dial, to give precisely accurate readings, if only its reading at any given value of the quantity measured, is consistently reproduced in subsequent determinations. The latter condition can never, of course, be fulfilled in practice, as all instruments are subject to more or less unaccountable and unsystematic variations under the conditions of ordinary use. Thus a weighing scale used to weigh the same load repeatedly, will never give identical successive readings of the weight, but will show more or less variation about a mean reading, which latter, however, is likely to be quite a definite and stable value, becoming more definite as the number of observations entering into the average is increased.

With these considerations in mind, it is seen that in the construction of a leather-measuring machine very precise results would be assured if it were possible to eliminate practically all the

variance, as the correction of the remaining inaccuracy would involve only the simple matter of regraduating the dial or changing the length of an adjustable lever or cam or similar element. The problem, then, is reduced to one of diminishing the variance to such an extent that the errors of all readings of the machine will lie within the established tolerance, or, as might perhaps be a more rational though less simple mode of specification, that the *average deviation* from exact reading shall not exceed a certain other, and, of course, smaller tolerance.

In order to select, then, from a group of several measuring machines, that type which can be expected to afford the most reliable results, the criterion should be reproducibility or invariance of reading rather than accuracy of reading in the ordinary sense of the term. As has been stated, all commercial measuring instruments are subject to sensible variation in reading, and while it is conceivably possible to adjust the average performance of the instrument over any considerable period of operation to such accuracy that no general or extensive aggregate error or economic loss would be engendered, nevertheless, to provide against large individual errors, and to prevent serious injustice in occasional, accidental cases, the basis of selection of the instrument should be the range of variation of reading at particular values of the quantity being measured, or the average deviation from the mean reading corresponding to particular values of the quantity being measured.

By way of example, it may be stated that differences as high as 4.3 per cent have been noted in the case of readings in the same series on the same area on one common type of leather-measuring machine. Two other machines gave extreme variations of 2.3 per cent and 1.3 per cent, respectively.

The accuracy of a measuring device depends upon the adjustment to which it was subjected by the maker and, within reasonable limits, the mean of its readings can by proper care at the time of test, be adjusted to be, at that time, practically coincident with the true value of the quantity measured. The deviation of successive observations from these mean readings, however, is not subject to improvement by adjustment, and in that sense is not the result of mere casual circumstances or accidents in the adjustment of the instrument.[5] It represents rather the effect of design and workmanship upon the readings, and forms, therefore, a

[5] See "The Concept of Resilience with Respect to Indicating Instruments," by the present author. Journal of the Franklin Institute, February, 1919; pp. 166–167.

criterion by which machines of diverse types can be differentiated, as compared with the accuracy of individual readings, which is best employed to differentiate between several machines of the same type and quality.

The problem in hand, then, in the case of leather-measuring machines is to select that type which is capable of most accurately reproducing its readings in successive measurements of the same area, and such selection can be made on the basis of a group of readings given by the instrument when it is operated repeatedly, using the same area standard.

This criterion may be expressed numerically by the use of the "average deviation of the readings from the mean" which, assuming a group of readings taken by successive operations of the machine on the same area, is obtained as follows: (1) Compute the average of the observations obtained by successive measurements of the same area made under the same conditions; (2) Compute the difference between each of the several observations and the average of the group. These differences are the deviations or departures of the several observations from the mean. The sum of all the deviations divided by the number of observations is the "average deviation from the mean."

This method of analysis permits the determination also of the probability or chance that any machine will give a preassigned deviation from the mean or average value of its successive readings, and also the probability that any deviation from the mean shall be greater or less than any given amount. For example, it has been deduced that one make of machine will commit a deviation or error of 1 per cent or more, about 60 times in 1000 operations, while a certain other make will commit an error of that magnitude about 360 times in 1000 operations, these conclusions applying to determinations made with a 10-square-foot test sheet of the later Bureau of Standards' design applied with its long axis moving perpendicularly to the common axis of the traversing wheels. By this method of calculation, very definite differences in performance were developed between three makes of machines investigated, their ratings on a scale of average deviation from mean reading being represented by the series 0.34, 0.42, 1.07; the smallest number, of course, which represents the smallest average deviation from the mean, corresponding to the highest rating as to repeating accuracy. The mean errors of the same three machines were, taken in the same order as the foregoing, 0.7 per cent, 0.6 per cent, 1.5 per cent.

To repeat, it may be said that the mean error could be diminished practically to zero by a suitable change in the adjustable parts of the machines, or, more generally, by recalibration of the dial. This would leave the machines comparable strictly upon the basis of the average deviation from the mean reading, which would necessarily, of course, be combined in the final decision, with numbers expressing excellence in respect to other qualities, such as smallness of errors due to overrun, width of tires, spacing of wheels, thickness of sheet, etc. Numerical expressions for all these effects can be obtained and a combination of these numbers into one number, the several components being suitably weighted according to the importance which each is considered to possess, will then be made, affording a single significant number, which may be called the figure of merit of the machine.

The following table gives the results of a series of variance determinations made on three leather-measuring machines, showing the steps in the calculation and the nature of the numerical results arrived at:

**TABLE 4.—Bureau of Standards Test of Three Leather-Measuring Machines at Danversport, Mass., Aug. 22, 1918**

[All determinations made with long axis of test area moving perpendicularly to common axis of traversing wheels. Test sheet used: Bureau of Standards type (Fig. 16)]

| | Machine I | | Machine II | Machine III[a] | | | |
|---|---|---|---|---|---|---|---|
| | [b] | [c] | [b] | 1 | 2 | 3 | 4 |
| Successive readings of the several machines on the same area standard | | | | | 10.01 | | |
| | 10.00 | 10.10 | 10.12 | 9.95 | 10.02 | 10.08 | 10.02 |
| | 10.02 | 10.24 | 10.05 | 10.08 | 9.97 | 10.20 | 10.02 |
| | 10.13 | 10.25 | 10.00 | 10.18 | 10.04 | 10.07 | 10.10 |
| | 10.07 | 9.87 | 10.06 | 10.07 | 10.03 | 10.09 | 10.06 |
| | 10.13 | 10.25 | 10.04 | 10.01 | 10.00 | 10.04 | 10.03 |
| | 10.13 | 10.05 | 10.07 | 9.97 | 10.00 | 10.09 | 9.93 |
| | 10.18 | 10.30 | 10.09 | 10.06 | 9.96 | 10.02 | 10.11 |
| | 10.02 | 10.06 | 10.10 | 10.13 | 10.07 | 10.07 | 10.02 |
| | 10.17 | 10.05 | 10.02 | 10.15 | 10.05 | 10.07 | 10.11 |
| | 9.93 | 10.10 | 10.13 | | 10.12 | | 10.03 |
| | | | | | 9.97 | | |
| Mean | 10.08 | 10.13 | 10.07 | 10.07 | 10.02 | 10.08 | 10.04 |
| Mean error, per cent | .92 | 1.53 | .08 | .84 | .37 | .78 | .57 |
| Average deviation, per cent | .70 | 1.07 | .34 | .61 | .35 | .31 | .43 |
| Extreme variation, per cent | 2.5 | 4.3 | 1.3 | 2.3 | 1.6 | 1.8 | 1.9 |

[a] 1, 2, 3, 4—Forty observations taken by the author, August, 1918.
[b] Ten observations taken by J. J. Cummings, March, 1918.
[c] Ten observations taken by the author on same machine in August, 1918.

| | | |
|---|---|---|
| Mean of 40 observations | | 10.05 |
| Average deviation, 40 observations | per cent | .42 |
| Extreme variation, 40 observations | do | 2.70 |
| Check measurements on the test sheet show that its actual area was | sq feet | 10.04 |

### 3. ACKNOWLEDGMENTS

In connection with this investigation it is a pleasure to acknowledge the hearty and effective cooperation which the author has received from a number of sources. H. M. Roeser, Assistant Physicist of the Bureau of Standards, who is a specialist in the theory of errors, has afforded most valuable cooperation in drafting and carrying out the methods for the calculation and numerical expression of the variability of leather-measuring machines. E. C. Laughlin, assisted by E. W. Shippee, V. A. De Castro, and T. M. Cockrill, all of the staff of the Bureau of Standards, carried out with painstaking care and accuracy, the very extensive series of measurements and calculations required to establish the areas of the six hides used as tentative reference standards in the early part of the investigation, as well as much of the computation involved in some of the later work regarding the errors due to overrun, etc. Both the National Boot & Shoe Manufacturers' Association and the National Tanners' Association have furthered the work in a most enthusiastic way, and especial mention is due, respecting the courtesies extended by W. H. Denham of the former and Walter Creese of the latter organization. J. J. Cummings, of the staff of the commissioner of weights and measures of the State of Massachusetts, lent continual assistance during the field work in Massachusetts, and took a number of observations which were needed in connection with the studies being made of the amount of the inherent variability of leather-measuring machines. Mr. Day, of the same office, also aided in the field work. To these and to the tanners, leather dealers, and shoe manufacturers who made possible the inspection of their measuring equipment and methods, and all others who have furthered the investigation, the author is happy to express appreciation on behalf of himself and the Bureau of Standards.

## IV. SUMMARY

The scant literature on the subject of leather-measuring machines is reviewed, and the facts which called for the carrying on of the present investigation are reported. The importance of the problem of leather measurement from the commercial point of view is indicated, as it underlies the sale of 900,000,000 square feet, or more than $400 000 000 worth of hides and skins annually in the United States. The principles of design involved in leather-measuring machines are set forth in detail with respect to the

kinds in common use. An analysis is made of the sources of the serious errors which commonly exist in commercial leather-measuring machines of the wheel type, including the effect of width of traversing wheel rim, of overrun of the wheelwork, of varying thickness of the material measured, of imperfections and mechanical complexity in the linkwork, etc. Attention is called to the fact that a number of the sources of error definitely favor overmeasurement, so that, on the whole, the common leather-measuring machines will tend to measure constantly in excess.

A design for standards of area, which eliminates the disadvantages of the simple rectangular and circular outlines hitherto employed in the testing of leather-measuring machines, is presented, and a complete outline of procedure for the conduct of performance tests on these machines is laid down. Distinction is drawn between accuracy which is evidenced as an invariable correctness of indication, and accuracy which appears as correctness in the mean value of variant indications, and it is shown that variancy of indication may be a far more serious fault than simple inaccuracy, since the latter can be corrected for by adjustment of the machine, while the former, generally speaking, can not. The paper indicates a means of obtaining a numerical comparison of measuring machines with respect to the variancy or lack of consistency in their readings, and gives in tabular form the results of variance tests on three wheel machines, showing typical calculations of the essential factors.

WASHINGTON, August 19, 1919.

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## No. 154

# DETERMINATION OF CELLULOSE IN RUBBER GOODS

BY

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*Bureau of Standards*

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By S. W. Epstein and R. L. Moore

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Discussion of proposed method | 4 |
| III. Details of method as proposed | 7 |
| IV. Results of analysis | 8 |
| V. Conclusions | 16 |


## I. INTRODUCTION

The chemist who still determines the rubber content of mixings by the difference method finds himself confronted from time to time with conditions that make an analysis by this method worthless. He finds ingredients present which are driven off in the ashing, yet are not included in the other determinations so that, unless these ingredients are determined separately, the figure for rubber hydrocarbon must necessarily be erroneous. One outgrowth of this condition was the development of a method for the determination of free carbon in rubber goods by A. H. Smith and S. W. Epstein of this Bureau.[1] Likewise it was found necessary to determine nitrogen by the Kjeldahl method in order to ascertain the quantity of glue in mixings. A great variety of rubber products which have cellulose impregnated with rubber in such a way that it can not be separated from it, come to the laboratory for analysis. Rubber sheeting, raincoat materials, balloon fabrics, and the wide variety of spread goods and frictioned fabrics represent a few of these. In addition there is the type of mixing which has fiber distributed throughout the compound, such as fiber soles, special light compounds, special packings. In order properly to evaluate these products it is evident that the fiber must be determined separately.

Further, the determination of cellulose in rubber presents a matter of primary importance to those engaged in checking up factory processes as well as those who are interested in competitors' products with the idea of duplication. The determination

[1] Technologic Paper 136, U. S. Bureau of Standards.

of cellulose gives a direct method to ascertain the amount of rubber compound which has been spread or calendered upon the fabric. It gives a ready method of studying frictioned stocks. Finally, in the reclaiming industry it is important to know whether or not the reclaiming process in a particular case removes all or a part of the fiber present.

## II. DISCUSSION OF PROPOSED METHOD

B. D'Porritt in his "Isolation and Examination of Rubberized Fabrics" [2] obtains the weight of fabric by dissolution of the rubber coating in paraffin. In cases where there are fillers, these are removed by special treatment before the fabric is weighed. In the presence of fillers not soluble in dilute acids, he determines the weight of cellulose by combustion. It has been our experience that considerable organic matter is left insoluble when solution of rubber is attempted by means of paraffin. It seems to us, therefore, that the results of the combustion could not be very reliable for this reason alone, without considering gas black which may be present and the possible varying nature of the fabric. The only method in the literature that we could find which makes any claims toward analyzing a vulcanized rubber compound for its cellulose content is one by H. G. Hillen,[3] who was interested in finding out whether or not the reclaiming process left considerable quantities of cellulose in the finished product. He ground the rubber sample extremely fine by special means, and allowed it to remain in copper-ammonia solution for from 6 to 10 hours. It was then filtered and the cellulose precipitated from the filtrate by the addition of sulphuric acid. This was then filtered out and weighed. Hillen stated that (1) only high-grade compounds can be analyzed by this method; (2) the sample must be ground very fine by special means in order to be reasonably certain that all of the cellulose will be removed from the rubber; (3) unless care is taken to keep the ammonia from being given off during the period of 6 to 10 hours, there is considerable danger of error; (4) there is danger of the cellulose being hydrolyzed if it is left in contact with the sulphuric acid for any length of time; (5) it is difficult to filter the voluminous, gelatinous precipitate of cellulose since it clogs up the Gooch filter. In conclusion he stated that the procedure is accurate enough only for industrial purposes.

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[2] Rubber Age and Tire News, 0, p. 386; Aug. 10, 1919.
[3] Gummi-Zeitung, Mar. 3, 1916.

In our opinion the method of Hillen could not be acceptable because of the presence of rubber, substitutes, and other organic material during the immersion in copper-ammonia. It is not improbable that precipitates are obtained, when the sulphuric acid is added, that are other than cellulose. But what is more important, it is an uncertain thing to attempt to remove cellulose from a rubber compound with which it has been intimately mixed by a process which can be likened unto extraction. Therefore it was decided that the rubber must first be removed before any attempt could be made to determine the cellulose by any procedure. The most convenient way to accomplish the removal of rubber from the sample was found to be through the use of cresol. Early experimentation with cresol (B. P. 198° C) had indicated that it would effect this solution at 160 to 185° C in from 2 to 4 hours, depending on the coefficient of vulcanization, and that the resulting solution after it had been diluted with petroleum ether (B. P. about 45 to 50° C) would allow the fillers to settle out in a very short length of time, after which it could be filtered easily and rapidly.

Samples of cotton, free from moisture, were immersed in cresol and allowed to remain for the maximum period of 4 hours at 185° C. The solution was diluted with petroleum ether and filtered. The weight of the washed and dried cellulose after this treatment was identical with the weight of sample taken.

The use of cresol was therefore adopted to remove the rubber as the first step in the method as outlined. From this point we proposed to remove the fiber, and determine it as the loss in weight occasioned by the process of solution. Obviously, all mineral fillers which would be affected by the reagents used to dissolve the cellulose would have to be removed beforehand. Likewise the reagents used to remove these fillers must not affect the cellulose.

It was found that 10 per cent hydrochloric acid when used to wash cellulose would not affect it in such a way as to produce a change in weight. However, if acid of higher concentration was used, the effect was considerable, even to the extent of causing a loss of 10 per cent of its weight. The 10 per cent hydrochloric acid removed a large part of the fillers in most cases so that the residue consisted of the practically insoluble fillers and the fiber. The choice of a procedure to remove the cellulose and record the loss in weight as cellulose with accuracy had to be directed from a

knowledge of a possible effect on the insolubles and the Gooch asbestos. Concentrated hydrochloric acid, concentrated sulphuric acid and strong sodium hydroxide had to be ruled out because of this. It was decided to rule out the copper-ammonia solution because of the uncertainty of completely dissolving the cellulose, and because of the comparatively long time required. The final result of consideration of the various cellulose solvents led conclusively to the choice of acetic anhydride. It was found that acetic anhydride to which has been added a small quantity of concentrated sulphuric acid, dissolves cellulose with surprising rapidity. This solution will be complete in 5 to 10 minutes even when large quantities of substance are treated. Our early experiments indicated that after 10 per cent hydrochloric acid had been applied to the fillers obtained from a rubber mixing, the acetylation mixture would have no effect upon the residue. This was confirmed in later work.

Samples of dried cotton were treated with varying mixtures of acetic anhydride and sulphuric acid at different temperatures, and the time was noted in which complete solution took place. The resulting solutions of cellulose were filtered through weighed Gooch crucibles, and the pads washed with hot 90 per cent acetic acid and then with acetone. In every case where there seemed to be complete solution, the weight of the Gooch before filtration and after was identical. A direct result of this work was the evidence that 90 per cent acetic acid and acetone removed all of the acetylation products from the pad. It was found that a mixture of acetic anhydride and concentrated sulphuric acid made up 30:1 was the best adapted for the acetylation and that as much as 1 g of cotton fiber could be dissolved in 20 cc of this mixture in less than 15 minutes at a temperature of 75° C.

Some difficulty was encountered with the first attempts to acetylate material directly in the Gooch crucible. The cause was traced directly to the loss of small quantities of finely divided fillers in the manipulation. As a result, several refinements had to be introduced. The asbestos pad was removed from the Gooch crucible, placed in a weighing bottle, dried, and weighed. The material was then transferred to the beaker in which the acetylation was to take place. After the reaction was completed, the solution was filtered through a freshly prepared Gooch containing a thick pad of asbestos. The liquid filters very easily, so that the thick pad does not slow up the operation. By carrying out the work as given it was found that no particles of material would run through.

## III. DETAILS OF METHOD AS PROPOSED

After having considered the essentials of a procedure for the determination of cellulose in rubber goods, the following method was devised:

Digest a 0.5 g sample of rubber in a 250 cc assay flask with 25 cc of freshly distilled cresol (B. P. 198° C) for 4 hours at 160 to 185° C. The digestion can be carried out on an electric hot plate, or better still in a constant-temperature oven. Allow the cresol to cool completely, and add 200 cc of petroleum ether (B. P. 45 to 50° C) very slowly and with constant agitation. After the solution has settled completely and the supernatant liquid is perfectly clear, filter through a Gooch crucible containing a fairly thick pad of acid-treated and ignited asbestos, and wash 3 times with petroleum ether. Wash at least 5 times with hot benzene and then once or twice with acetone. Treat the contents of the flask with hot 10 per cent solution of hydrochloric acid, and transfer the entire contents of the flask to the Gooch crucible with the aid of a "policeman." Care must be taken in adding the first portion of acid to the Gooch, since, in the presence of carbonates, the effervescence which ensues may cause some of the material to be lost. It is best to add the acid a few drops at a time until there is no more effervescence. Continue to treat with hot 10 per cent solution of hydrochloric acid until the pad has been washed at least 10 times. Wash the pad free from chlorides with boiling water, and run small portions of acetone through it until the filtrate comes through colorless. Treat with a mixture of equal parts of acetone and carbon bisulphide until the solvent is no longer colored. Wash with alcohol, and dry for 1 hour and 30 minutes at 105° C. Remove the pad from the crucible with the help of a pair of sharp-pointed tweezers, and place it in a weighing bottle that is large enough to contain a 25 cc Gooch crucible or the size crucible that is being used. Use the underneath portions of the pad as a swab to clean the sides of the crucible. If necessary, moisten this asbestos with a little alcohol, since this will facilitate the complete removal of material which sometimes adheres tenaciously. Place the weighing bottle and contents in the drying oven for about 15 minutes, cool and weigh. Call this weight *A*.

Transfer the contents of the weighing bottle to a 50 cc beaker, taking precautions that no material is lost during the transfer, or allowed to remain in the weighing bottle. Add 15 cc of acetic anhydride and 0.5 cc of concentrated sulphuric acid, and allow to

digest for 30 minutes at 75° C. The steam bath can be conveniently used for this purpose. After the mixture has cooled completely dilute with 25 cc of 90 per cent acetic acid and filter through a weighed Gooch containing a thick pad of properly prepared asbestos. To guard against traces of material being carried through it is absolutely essential that this filtration, as well as the ones to follow, be very slow, and that only gentle suction be used. Wash with hot 90 per cent acetic acid until the filtrate comes through absolutely colorless, and than wash at least 4 times more. Wash about 5 times with acetone. After having taken care that all of the material has been washed out of the beaker in which the acetylation took place, remove the crucible from the funnel, clean the outside thoroughly, place it inside of the same weighing bottle that was used to weigh the pad, and dry for 2 hours at 150° C. Cool and weigh. Call this weight *B*.

Weight of Gooch crucible + weight *A* − weight *B* = loss due to acetylation or cellulose.

NOTE.—It is essential that all reagents given above be of chemically pure quality, and be filtered before using.

When large numbers of determinations were carried out according to the above procedure, it was found practical to distil the filtrates, and in this way recover a large part of the solvents used. The combined filtrates containing petroleum ether, benzene, and cresol were distilled on the steam bath to recover the petroleum ether. The benzene was recovered as the temperature was raised. Finally, the water condenser was replaced by an air condenser and the cresol distilled out at about 195 to 200° C. This distillate was usually only slightly yellow.

Likewise the filtrates from the acetylation, which contain acetic anhydride, acetic acid, and small quantities of sulphuric acid, were collected and distilled. The distillate was collected between 105 and 115° C, and was used for washing to take the place of the 90 per cent acetic acid called for in the proposed method.

## IV. RESULTS OF ANALYSIS

In order to ascertain the reliability of the method as proposed a number of representative compounds were prepared, and the cellulose content determined by means of it. In the preparation of these compounds the fiber as well as all of the fillers were dried before weighing out the batch.

**Stocks Containing No Cellulose**

| G–2: | Per cent |
|---|---|
| Para | 43.0 |
| Glue | 7.0 |
| Whiting | 35.0 |
| Lampblack | 7.0 |
| Sulphur | 3.0 |
| Litharge | 3.0 |
| Magnesia | 2.0 |
| Fiber | None. |
| | 100.0 |

| B. S. 53: | |
|---|---|
| First latex | 48.0 |
| Zinc oxide | 22.0 |
| Litharge | 24.0 |
| Sulphur | 2.0 |
| Lampblack | 4.0 |
| Fiber | None. |
| | 100.0 |

| S. B. 5: | |
|---|---|
| Plantation crêpe | 60.0 |
| Golden antimony | 5.0 |
| Zinc oxide | 10.0 |
| Lithopone | 10.0 |
| Thiocarbanilide | 2.0 |
| Sulphur | 3.0 |
| Iron oxide | 10.0 |
| Fiber | None. |
| | 100.0 |

Blank determinations made on the above mixings showed losses due to acetylation of 0.0006 g, 0.0007 g, and 0.0006 g, respectively.

The results obtained indicate that of the material which was insoluble in 10 per cent hydrochloric acid, and was present throughout the acetylation, nothing was dissolved by the acetylation reagents. Evaporation and ignition of the filtrate revealed no residue. It is evident that the method will not give misleading results, and that no cellulose will be indicated by it when it is not present.

**Stocks Containing Cellulose in the Form of Cotton Fiber**

| C–1: | Per cent |
|---|---|
| Smoked sheet | 50.0 |
| Zinc oxide | 30.0 |
| Whiting | 6.0 |
| Chrome green | 3.0 |
| Sulphur | 3.0 |
| Cotton fiber | 8.0 |
| | 100.0 |

| C–2: | |
|---|---|
| Smoked sheet | 70.0 |
| Golden antimony | 15.0 |
| Calcium sulphate | 4.0 |
| Sulphur | 6.0 |
| Cotton fiber | 5.0 |
| | 100.0 |

| C–3: | Per cent |
|---|---|
| Plantation | 59.0 |
| Gas black | 5.0 |
| Zinc oxide | 30.0 |
| Sulphur | 5.0 |
| Cotton fiber | 1.0 |
| | 100.0 |

| C–4: | |
|---|---|
| First latex | 40.0 |
| Mineral rubber | 5.0 |
| Gas black | 15.0 |
| Zinc oxide | 30.0 |
| Magnesium oxide | 2.0 |
| Magnesia, light | 3.0 |
| Sulphur | 2.0 |
| Cotton fiber | 3.0 |
| | 100.0 |

**By Analysis**

| | Per cent |
|---|---|
| C–1: Cellulose | 7.96 |
| C–2: Cellulose | 4.86 |
| C–3: Cellulose | 0.98 |
| C–4: Cellulose | 2.93 |

The above results indicate clearly without further discussion that by this method it is easy to determine widely varying amounts of cotton fiber very accurately even when accompanied by a miscellaneous collection of mineral fillers in the rubber compound. Attention is called to C–4, where 15.0 per cent of gas black was present. It was possible to get good figures on cellulose because the weighings were all made in weighing bottles and, therefore, no error was introduced by the absorption of quantities of moisture by the large amount of carbon. It was found to be absolutely impossible to get reliable results at all unless this was strictly observed.

In order to illustrate how the method applies to the checking up of calendered goods, two samples of fabric were run through the calender in such a way that the final products should be as nearly 30 and 50 per cent cloth, respectively, as possible.

The sample which was intended to be 30 per cent fabric analyzed 29.1 per cent cellulose.

The sample which was intended to be 50 per cent fabric analyzed 48.5 per cent cellulose.

Seven reclaims of unknown cellulose content were analyzed, and a great variation in the cellulose content of the different grades was uncovered. The results of analysis ranged from 0.8 per cent to the high value of 11.36 per cent. The wide range of values furnishes conclusive evidence of the importance of checking up the cellulose content of reclaims by both the reclaimer and the purchaser.

**Results of Determinations of Cellulose in Reclaims**

| Reclaim | Cellulose content | | |
|---|---|---|---|
| | Per cent | Per cent | Per cent |
| No. 1 | 11.36 | 11.36 | 11.34 |
| No. 2 | 8.20 | 8.22 | 8.32 |
| No. 3 | 3.18 | 3.22 | ..... |
| No. 4 | 3.30 | 3.26 | ..... |
| No. 5 | 3.24 | 3.24 | ..... |
| No. 6 | 5.2 | 5.0 | ..... |
| No. 7 | 0.8 | 0.74 | ..... |

The presence of such large quantities of cellulose in some reclaims shows the necessity of looking for cellulose in finished rubber goods of a grade in which reclaim might logically be expected. Its presence furnishes a very good indication that reclaim was used in the mixing. The following furnishes a very good illustration of this. Four samples of what appeared to be

high-grade rubber and to be free from reclaim were submitted for test and analysis. Cellulose was determined in them with the following surprising results:

| Sample | Cellulose | |
|---|---|---|
| | Per cent | Per cent |
| A | 1.9 | 1.88 |
| B | 2.0 | 1.97 |
| C | 1.5 | 1.5 |
| D | 2.73 | 2.74 |

These results were obviously of great assistance in evaluating the sample, and in addition brought the figure for rubber hydrocarbon in the report nearer to its correct value.

The presence of ground leather in a rubber sample in which cellulose is to be determined does not influence the result obtained upon acetylation. When leather is digested in cresol at 185° C it is detanned. The gelatin that is liberated dissolves in the cresol, while, in the case of vegetable-tanned leather the tannin that is split off is decomposed by the heat into phloroglucinol, carbon dioxide, and metagallic acid.[4] The latter is a dark-colored, nonvolatile residue, insoluble in water and acids, and averages 15 per cent of the leather digested. It is easily dissolved when it is washed alternately with a hot 2 per cent solution of sodium hydroxide and a 10 per cent solution of hydrochloric acid. The resulting solution readily reduces potassium permanganate. Since cellulose is not affected by 2 per cent sodium hydroxide solution, it is practical to remove the metagallic acid which was formed from leather present in the mixing by treatment with this solution and then to acetylate in the manner outlined here. When the presence of leather is suspected, it is necessary to wash with a 2 per cent solution of sodium hydroxide and if a deep brown extract is obtained, these washings must be continued, alternating with 10 per cent solution of hydrochloric acid, until the washings are colorless. The pad is then washed with 10 per cent hydrochloric acid, etc., as given in "Details of Method as Proposed."

The determination of cellulose in compound 8 was carried out as given under "Details of Method as Proposed," except that the pad was washed alternately with a hot 2 per cent solution of sodium hydroxide and a 10 per cent solution of hydrochloric acid before acetylating, in order to remove the leather residue, metagallic acid, as explained above.

[4] Allen's Commercial Organic Analysis.

**EXAMPLE 1.—Compound Containing Leather and Substitute**

| Compound 8: | Per cent |
|---|---|
| Smoked sheet | 45.0 |
| White substitute | 5.0 |
| Zinc oxide | 29.0 |
| Leather | 13.0 |
| Cotton (cellulose, 4.7; moisture, 0.3) | 5.0 |
| Sulphur | 3.0 |
| | 100.0 |

Cellulose by acetylation, 4.6 per cent.

This test analysis indicates clearly that the presence of considerable amounts of leather does not affect the determination of cellulose.

Other substances which must be considered here are wood, jute, and cork, since these may also be expected in certain types of rubber mixings. When these substances are digested in cresol at 185° C for four hours, they undergo marked changes in composition, and in the case of cork there is decided blackening and change of physical structure. The changes are explained somewhat when one recalls that wood, jute, and cork are considered as incrusted celluloses. They consist of some form of cellulose combined with a noncellulose constituent which may be either of the nature of lignin in the case of the ligno-celluloses such as wood and jute, or a fatty substance in the case of the adipo-celluloses, of which cork is an example. The treatment in cresol at 185° C seems to remove these incrusting substances. In the case of wood and jute there seemed to be complete delignification, for the residue was almost pure white, responded to all the tests for celluloses, and acetylated completely.

The loss in weight that corresponded to delignification ranged from 35 to 55 per cent, and seemed to depend upon the age of the growth from which the fiber was obtained. In the case of cork the loss in weight ranged from 50 to 60 per cent. The residue was very much altered, and no longer exhibited its corky character. This material acetylated incompletely, and left a residue of about 10 per cent of the weight of original sample. Obviously, it is not possible to obtain correct figures for wood, jute, and cork by the method outlined here. The acetylation result represents usually but 50 per cent of the amount of each of these present.

It was found by experiment that the power to delignify wood and jute, and to break down cork structure, did not seem to lie in the cresol itself, but in the temperature at which they were treated, for other liquids were used, and the same phenomenon was noted whenever the temperature rose above 130° C. Below

this temperature there was no noticeable change. Samples of wood, jute, and cork, treated with cresol for 16 hours at 120° C, apparently were unaffected. Wood and jute at the end of this treatment did not give any of the tests for cellulose but responded to those for lignin. When dipped into 1½ per cent alcohol solution of phloroglucinol, and touched with a drop of dilute acid, these fibers were colored red.

Knowing that vulcanized rubber is dissolved in cresol at 120° C in 16 hours, some experiments were carried out in order to ascertain whether a more accurate determination of these fibers could be obtained. It was found that—

TABLE 1

| | Wood | Jute | Cork | Leather |
|---|---|---|---|---|
| Material remaining after 16 hours, immersion in cresol at 120° C | Per cent 98 | Per cent 96 | Per cent [illegible] | Per cent [illegible] |
| Material remaining after having been washed with hot 10 per cent solution of hydrochloric acid and water | 95 | 91 | 91 | 70 |
| Acetylation | 95 | 90 | 21 | 70 |

The treatment with cresol at 120° C evidently removed some moisture, fats, greases, etc., from these materials, but did not affect the fundamental substance. The washings with a 10 per cent solution of hydrochloric acid and water removed the "water solubles" from the leather. These are usually glucose, Epsom salts, soluble tannin, and run from 5 to 30 per cent of the leather sample. In the cases of wood, jute, and cork it is uncertain just what was removed.

In the cases of wood and jute, it is clear that a comparatively accurate estimation of their quantity can be obtained by using the modified procedure, in which the temperature of 120° C is used in place of 185° C in order to dissolve the rubber.

The acetylation figure includes about 70 per cent of the leather, since all attempts intended to remove it result in an attack upon the lignin of wood and jute, which are sensitive to bromine water, hot sodium hydroxide, etc.

In the absence of wood, jute, and cork an approximation of the amount of leather present can be obtained in the following manner: Digest one sample at 185° C with cresol, remove the leather decomposition products, by means of a 2 per cent solution of sodium hydroxide as given above, and acetylate. The result gives cellulose alone. Another sample is digested at 120° C for 16 hours in cresol, washed with acid, and acetylated. The result

is cellulose and about 70 per cent of the leather. Subtracting from this figure the result obtained above, a result is obtained which can be taken to represent about 70 per cent of the total leather present.

**EXAMPLE 2.—Approximation of Leather Content**

| Compound 8: | Per cent |
|---|---|
| Smoked sheet | 45.0 |
| White substitute | 5.0 |
| Zinc oxide | 29.0 |
| Leather (moisture, 1.2; leather, 11.8) | 13.0 |
| Cotton (moisture, 0.3; cellulose, 4.7) | 5.0 |
| Sulphur | 3.0 |
| | 100.0 |

Example 2: By acetylation 12.2 per cent. (Calculated from Table 1, this result should be (11.8) (70 per cent) + 4.7 = 12.9 per cent.)

Example 1: By acetylation 12.2 per cent − 4.6 per cent=7.6 per cent (using 185° C. for digestion in cresol and removing the leather; represents approximately 70 per cent of the leather or 10.9 per cent leather.)

The actual amount of leather is 11.8 per cent, so that 10.9 per cent is to be considered a fair approximation.

Going back to Table 1 it is seen that 21 per cent of cork is acetylated, and that about 70 per cent remains behind on the Gooch pad. This constitutes a partial separation of cork from wood, jute, and leather, since these materials leave no residue after acetylation. The separation, detection, and approximation of cork works out as follows: Acetylation removes wood, jute, and leather, and leaves a residue from the cork which is about 70 per cent of the sample taken. This residue is digested for 1 hour on the steam bath in a 2 per cent solution of sodium hydroxide. It is then filtered through a weighed Gooch, washed alternately with strong bromine water and the hot 2 per cent solution of sodium hydroxide, and finally with a 10 per cent solution of hydrochloric acid. The cork residue is completely removed, and is determined as the loss in weight. It constitutes about 70 per cent of the cork. If no loss in weight is obtained, it means that no cork was present in the sample.

**EXAMPLE 3**

| Compound 9: | Per cent |
|---|---|
| Smoked sheet | 38.0 |
| Brown substitute | 5.0 |
| Cork | 10.0 |
| Zinc oxide | 42.0 |
| Vaseline | 2.0 |
| Sulphur | 3.0 |
| | 100.0 |

By acetylation 1.9 per cent. (Calculated from Table 1, this should be 2.1 per cent.)

The residue after acetylation was treated with a 2 per cent solution of sodium hydroxide and bromine water as given above,

and showed a loss in weight of 6.7 per cent. Considering this as 70 per cent of the cork, the approximation of 9.8 per cent is obtained.

**EXAMPLE 4**

| Compound 10: | Per cent |
|---|---|
| Smoked sheet | 45.0 |
| Wood pulp | 7.5 |
| Cork | 7.5 |
| Pine tar | 3.5 |
| M. R. X | 2.0 |
| Zinc oxide | 20.0 |
| Magnesia usta | 8.0 |
| Lampblack | 4.0 |
| Sulphur | 2.5 |
| | 100.0 |

By acetylation 9.0 per cent. (Calculated from Table 1, this should have been 8.7 per cent.)

The residue after acetylation when treated to remove the cork, as given above, showed a loss in weight of 5.0 per cent. Considering this as 70.0 per cent of the total, an approximation of 7.1 per cent is obtained.

**EXAMPLE 5.—Stock Containing Jute**

| Compound 11: | Per cent |
|---|---|
| Smoked sheet | 36.0 |
| Litharge | 6.5 |
| Zinc oxide | 43.0 |
| Magnesia usta | 2.5 |
| Jute | 10.0 |
| Sulphur | 2.0 |
| | 100.0 |

By acetylation 9.0 per cent. (Calculated from Table 1, this should have been 9.0 per cent.)

**EXAMPLE 6.—Stock Containing Wood**

| Compound 12: | Per cent |
|---|---|
| Smoked sheet | 50.0 |
| Wood pulp | 17.0 |
| Glue | 10.0 |
| Zinc oxide | 20.0 |
| Aluminum flake | 4.4 |
| Sulphur | 2.6 |
| | 100.0 |

By acetylation 12.4 per cent. (Calculated from Table 1, this should have been 12.35 per cent.)

**EXAMPLE 7.—Stock Containing Cotton, Jute, and Leather.**

| Compound 13: | Per cent |
|---|---|
| Smoked sheet | 40.0 |
| Zinc oxide | 29.5 |
| Magnesium carbonate | 4.0 |
| Red oxide of iron | 4.0 |
| Yellow ochre | 8.0 |
| Cotton | 4.0 |
| Jute | 4.0 |

Compound 13—Continued.

| | |
|---|---|
| Leather | 4.0 |
| Sulphur | 2.5 |
| | 100.0 |

By acetylation 10.3 per cent. (Calculated from Table 1 this should have been 10.4 per cent.)

In compound 11 and 12, where jute and wood are present alone, a fair determination is possible. In compound 13, where jute, leather, and cotton are all present, a combined figure is obtained which is 1.9 per cent under the total actually present. We have found it impossible to determine each separately. In our opinion the best that can be done is to identify the fibers by satisfactory stains and microscopic examinations, and to determine them collectively, as near as is possible, by acetylation. The rubber content is determined in such cases by the use of rubber solvents at a temperature not over 130° C and the estimation of total fillers.

## V. CONCLUSIONS

1. A method is presented which is readily applicable to the determination of fabric in rubber sheeting, raincoat materials, waterproofed fabrics, spread goods, frictioned and calendered fabrics in general. The results which are obtained by this method have been found to be accurate, by analysis of known compounds. The method has been shown to be useful in the detection and determination of cellulose in reclaims.

2. The presence of leather in mixings is shown not to interfere with determination of cellulose.

3. In the analysis of light, cheap compounds such as rubber soles where wood, jute, cork, and leather may be present, it is found desirable to digest sample at 120° C in cresol for 16 hours, in order to keep these fibers intact. Acetylation obtains 95 per cent of the total wood, 90 per cent of the total jute, 21 per cent of the total cork, and 70 per cent of the leather.

4. The amount of cork present in a mixing can be approximated by removing unacetylated cork residue, and considering this as 70 per cent of the total.

5. In the absence of jute, wood, and cork, it is shown that the amount of leather may be estimated approximately.

6. The problem of separately determining wood, jute, and leather in a mixing has not been solved.

WASHINGTON, October 23, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 155

## CEMENTS FOR SPARK-PLUG ELECTRODES

BY

HOMER F. STALEY, Metallurgical Ceramist

*Bureau of Standards*

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By Homer F. Staley

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Properties of the materials employed | 4 |
| (*a*) Electrode wires | 4 |
| (*b*) Porcelain | 4 |
| (*c*) Cements | 5 |
| III. Tests of various cements | 5 |
| (*a*) Sodium silicate and powdered silica | 6 |
| (*b*) Sodium silicate and barium sulphate | 6 |
| (*c*) Sodium silicate and aluminum oxide | 7 |
| (*d*) Sodium silicate and calcined kaolin | 7 |
| (*e*) Sodium silicate and raw kaolin | 7 |
| IV. Relation of the use of cements to the failure of spark plugs for mechanical reasons | 8 |
| (*a*) Breakage of porcelains | 8 |
| (*b*) Attempts to use glass seals | 8 |
| (*c*) Gas leakage | 9 |
| (*d*) Spark plugs with mechanical seals | 10 |
| V. Summary | 10 |


## I. INTRODUCTION

Considerable trouble has been experienced in the operation of airplane engines, due to breaking of the central electrode wires in spark plugs at the point where it enters the porcelain. For this reason the Bureau of Aircraft Production, under date of August 19, 1918, requested the Bureau of Standards to investigate this problem.

Examination of numerous broken spark plugs showed that at the point of failure the central electrode wire was oxidized practically through its cross section. This oxidation extended up into the spark plug a variable distance, depending upon the permeability of the cement with which the wire was surrounded. In some cases the cement had melted and run down along the wire. It was apparent from the nature of the failures that, in order to study the problem thoroughly, the properties of the electrode wire, porcelain insulator, and the cement used to secure the wire to the insulator, must be investigated.

## II. PROPERTIES OF THE MATERIALS EMPLOYED

(*a*) ELECTRODE WIRES.—The material most commonly used for central electrodes in spark plugs is known as 97 per cent spark point nickel wire. In the particular type of plug which gave trouble, the entire central electrode was of this material. The following are typical analyses:

**Composition of Wire**

| | | |
|---|---|---|
| Laboratory No. | 47134 | 47135 |
| Nickel[a] ..... per cent.. | 97.0 | 96.9 |
| Manganese ..... do.... | 1.5 | 1.6 |
| Iron ..... do.... | .8 | .9 |
| Copper ..... do.... | .4 | .2 |

[a] Contains cobalt, probably as much as 1 per cent. Some wires contain as much as 0.25 per cent silicon.

The thermal expansion of this wire as determined by the Bureau is given below:

**Thermal Expansion of Wire**

| Temperature interval | Average coefficient |
|---|---|
| 25 to 200 C | $14 \times 10^{-6}$ |
| 200 to 400 C | 16 |
| 400 to 600 C | 16 |
| 600 to 840 C | 20 |
| 25 to 840 C | 17 |

(*b*) PORCELAIN.—For making porcelain insulators, one spark plug manufacturer uses a modification of Bureau of Standards body No. 152, the thermal expansion of which is as follows:

**Thermal Expansion of Porcelain**

| Temperature interval | Average coefficient |
|---|---|
| 30 to 200 C | $3.36 \times 10^{-6}$ |
| 200 to 400 C | 3.36 |
| 400 to 520 C | 4.19 |
| 30 to 400 C | 4.78 |
| 30 to 520 C | 3.81 |
| | 4.06 |

This porcelain is of a special type developed by the ceramic division of the Bureau and will be described in a paper to be prepared by that division. In addition to low coefficient of expansion, it is remarkable for its comparatively great mechanical strength.

Another manufacturer uses porcelain having the following thermal expansion.

| Temperature interval | Average coefficient |
|---|---|
| 24 to 200 C | $5.7 \times 10^{-6}$ |
| 200 to 400 C | 6.7 |
| 400 to 540 C | 8.4 |
| 24 to 540 C | 6.8 |

(*c*) CEMENTS.—It developed through correspondence with various manufacturers that most of the cements used between wire and porcelain consisted of mixtures of silicate of soda with finely powdered solids, which were supposed to be chemically inert. Barium sulphate was the solid used by the manufacturer whose plugs gave the most trouble, while another maker, whose plugs are used in large quantities for airplane work, employed finely ground silica. Silicate-of-soda cements are advantageous for this work because they are cheap, can be worked cold, and are gas tight at low temperatures.

## III. TESTS OF VARIOUS CEMENTS

To determine the effect of various cements on electrode wires, mixtures were made of silicate of soda and typical powdered materials. Small pellets of these mixtures were worked around commercial nickel electrode wires, and after drying at 120° C., the wires and adhering pellets were heated in an oxidizing atmosphere to 500° C and then to 1000° C. These temperatures probably limit the range of temperatures attained at the tip of the porcelain of a spark plug in an airplane engine in operation. After cooling, the pellets were broken off and the wire beneath them examined. The results for the heating to 1000° C are given in Table 1. In the heating to 500° C the effect of the various compositions was not so marked but the relative effects were substantially the same.

TABLE 1.—Effect of Cements on Electrode Wires

| Cement No. | Sodium silicate 40° Baumé, cubic centimeters | Water, cubic centimeters | Solid | | Effect of heating to 1000° C | |
|---|---|---|---|---|---|---|
| | | | Grams | Kind | Oxidation | Description |
| 1 | 5 | 5 | 30 | Powdered silica | Very bad | Hard, strong, slightly porous; part of material had run down the wire. |
| 2 | 10 | ..... | 30 | ....do | ....do | Do. |
| 3 | 5 | 2 | 30 | Barium sulphate | Eaten through | Part of material had melted and run down wire, leaving a hard blue mass behind. |
| 4 | 7 | ..... | 30 | ....do | ....do | Do. |
| 5 | 5 | 5 | 30 | Kaolin | None | Hard, strong; very slightly porous. |
| 6 | 10 | ..... | 30 | ....do | ....do | Hard, strong; not porous. |
| 7 | 5 | 9 | 15<br>15 | ....do<br>Aluminum oxide | Very bad | Soft, weak, porous. |
| 8 | 10 | 4 | 15<br>15 | Kaolin<br>Aluminum oxide | ....do | Do. |

**TABLE 1.—Effect of Cements on Electrode Wires—Continued**

| Cement No. | Sodium silicate 40° Baumé, cubic centimeters | Water, cubic centimeters | Solid | | Effect of heating to 1000° C | |
|---|---|---|---|---|---|---|
| | | | Grams | Kind | Oxidation | Description |
| 9 | 5 | 13 | 30 | Aluminum oxide..... | Very bad..... | Soft, powdery mass. |
| 10 | 10 | 8 | 30 | .....do..... | .....do..... | Do. |
| 11 | 10 | 12 | 30 | Kaolin calcined at 500° C. | .....do..... | Hard, weak, porous. |
| 12 | 10 | 16 | 30 | Kaolin calcined at 750° C. | .....do..... | Do. |
| 13 | 10 | 14 | 30 | Kaolin calcined at 1000° C. | .....do..... | Soft, weak, porous. |
| 14 | 10 | 12 | 30 | Kaolin calcined at 1250° C. | .....do..... | Medium, hard weak, porous. |
| 15[a] | ..... | ..... | ..... | ..... | .....do..... | |
| 16[b] | ..... | ..... | ..... | ..... | Slight..... | |

[a] Wire dipped in 40° Baumé sodium silicate. [b] Clean wire.

(*a*) SODIUM SILICATE AND POWDERED SILICA.—From Table 1, it appears that the solids used do not act simply as inert materials. Hydrated sodium silicate alone bakes at temperatures well below 500° C to sodium-silicate glass. The composition of this glass is approximately 25 per cent $Na_2O$ and 75 per cent $SiO_2$. Its constitution, as that of all glasses, is unknown. It can be represented best by the formula $Na_2O\ x\ SiO_2$. Since sodium oxide is capable of forming glasses with widely varying amounts of silica, the reaction of sodium silicate with powdered silica consists of the solution of the finest particles of silica and the formation of a glass higher in silica than the original sodium-silicate composition. That the glass dissolved some oxide of nickel was shown by its bluish color. This glass must have been quite fluid, for the bulk of it ran down the wire, leaving behind a porous mass of silica grains coated and cemented together by thin films of glass.

(*b*) SODIUM SILICATE AND BARIUM SULPHATE.—Seger[1] has shown that molten sodium-silicate glass and barium sulphate react to form a glass consisting for the most part of barium silicate and glass gall made up largely of fused sodium sulphate. We may assume that this is what happened in cements Nos. 3 and 4. The formation of molten sodium sulphate accounts for the marked attack of this composition on the wire forming the electrode. The action of this mixture when heated readily explains the trouble arising in its use as cement for electrode wires in airplane engines.

[1] Collected Writings of Herman A. Seger, 2, p. 636, published by Chemical Publishing Co., Easton, Pa.

(*c*) SODIUM SILICATE AND ALUMINUM OXIDE.—A reaction took place in the cold between the sodium silicate and the precipitated aluminum oxide used in several of the cements as soon as they were blended. The resulting product was a rather friable, porous mass resembling plaster of Paris and entirely different from the hard vitreous-coated masses obtained when sodium silicate is mixed in the cold with inert substances such, for instance, as powdered silica. The action may have consisted of the formation of sodium aluminate or of sodium-aluminum silicate.

(*d*) SODIUM SILICATE AND CALCINED KAOLIN.—A similar action, but not so marked, seems to have taken place in the cold with calcined kaolin. When kaolins are calcined to temperatures between 450 and 1000° C they lose their two molecules of water and undergo a decrease in specific gravity; they also became much more active chemically in the cold than uncalcined kaolin.[2] This chemical activity is shown by the fact that calcined kaolin reacts with hydrated lime to form pozzuolanic cement and that it is much more soluble in acids than uncalcined kaolin.[3] When brought into contact with a strongly alkaline substance such as sodium silicate, calcined kaolin reacts quite rapidly to form a friable, porous mass.

As shown in the table, the porosity of the masses containing precipitated alumina and of those containing kaolin calcined at temperatures between 500 and 1000° C was retained on heating, the result being porous masses of little strength. The kaolin calcined at 1250° C had been rendered more nearly inert and when blended with sodium silicate gave products with properties midway between those of mixtures containing kaolin calcined at lower temperatures and of those made with the use of practically inert powdered silica.

(*e*) SODIUM SILICATE AND RAW KAOLIN.—Compositions made of mixtures of raw, or uncalcined, kaolin with sodium silicate were superior to others in that they did not fuse and were but slightly porous, thus protecting the electrode wires from oxidation. Raw kaolin is an extremely fine-grained substance which does not react in the cold with sodium silicate with the formation of a porous mass, as do precipitated alumina and calcined kaolin, but forms mixtures that dry to hard nonabsorbent masses. On heating such a composition water is driven off from both the sodium silicate and the kaolin and the remainder bakes to an impervious porcelain-like mass. The mechanism of this action is probably similar to that operating in the vitrification of a piece of porcelain, consisting of

[2] Knote, J. M., Trans. Am. Cer Soc., 12, pp. 226–235.

[3] Knote, J. M., loc. cit. Bleininger, A. V., Manufacture of Hydraulic Cements, Geological Survey of Ohio, fourth series, Bull. 3, p. 25.

the formation of a viscous glass, the coating of the grains of unfused materials by this glass due to surface tension forces, the drawing together of the unfused particles by the same forces, and finally the congealing of the glass as the mixture is cooled.

No doubt complex chemical reactions are involved in the above process but we are no more able to write these reactions than we are those taking place in the formation of a piece of porcelain or a pot of molten glass. From the standpoint of utility as cement for spark plug electrodes, the important points are that there is no reaction in the cold and that the glassy portion of the mixture at no stage of the process becomes sufficiently fluid to flow away from the unfused portion, and thus yields a nonporous instead of a porous substance. This is unquestionably due to the gradual assimilation into the glass of a portion of the alumina and silica of the kaolin. It is well known that the addition of either of these substances to alkaline glasses tends to produce greater viscosity.

## IV. RELATION OF THE USE OF CEMENTS TO THE FAILURE OF SPARK PLUGS FOR MECHANICAL REASONS

(*a*) Breakage of Porcelains.—The relation of the cement to the cracking of porcelains was clearly demonstrated on the occasion of a visit made by a representative of the Bureau to a spark-plug factory. In this plant porcelains were subjected to a sudden heating test, in which the tip of the porcelain was placed in the flame of a Meker burner. The porcelains were uniformly passing this test. When it was suggested that porcelains containing electrodes cemented in place be tested in the same manner, it was found that 45 per cent of the porcelains cracked. In the 55 per cent of plugs that did not fail, either cement was absent from around the wire near the tip of the porcelain or else it softened and gushed out of the hole. As the result of actual engine tests of complete plugs at the Bureau, it has been found in general that in the cracked plugs the cement is holding well and that plugs in which the porcelain is not cracked generally leak around the electrode wire. These failures are due in many cases, apparently, to the difference in coefficient of thermal expansion between the porcelain and nickel wire which sets up so high a stress between the two parts of the plug that either the porcelain or the cement has to give way.

(*b*) Attempts to Use Glass Seals.—Attempts were made to seal the wires into porcelains after heating by means of glasses, ranging in coefficient of thermal expansion from that of the

porcelain to that of the wire. None of these attempts was successful, for, in cooling, the glass pulled away either from the porcelain or from the wire and the spark plugs leaked badly. From a knowledge of the technique used in sealing metal into glass for various purposes, we know that it would be possible to use glass seals for electrode wires in at least two ways. One method would depend on having about the same coefficient of thermal expansion in porcelain, glass used for sealing, and electrode wire. Another would employ porcelain and glass of the same coefficient and seal this glass to metal electrodes or portions of electrodes of such thin cross section and consequent low mechanical strength that they would expand and contract with the glass. The use of either of these two methods of spark plug construction would involve various questions of heat conductivity, electrical resistance, kind of spark produced, etc., a discussion of which lies beyond the scope of this paper.

**TABLE 2.—Gas Leakage Around Electrode Wires in Spark Plugs that Had Been Used for 1¾ Hours in a Liberty Engine**

| Condition of porcelain | Gas leakage | Loose electrode wires | Wires easily pulled out |
|---|---|---|---|
| 12 broken [a] | 6 bad | 4 | 1 |
| | 6 none | None. | None. |
| 28 not broken | 17 bad | 12 | 9 |
| | 8 moderate [b] | 3 | 2 |
| | 3 none | None. | None. |

[a] Part of these may have been broken while the plugs were being removed from the engines.
[b] More than 0.2 cm³ per second.

(*c*) Gas Leakage.—The subject of gas leakage of spark plugs in relation to failure of the central electrode has also been studied. While considerable work has been done in determining the gas leakage of new plugs in view of the above results it appeared advisable to determine leakage on plugs that had been used in an airplane engine. In Table 2 are given the results of examination of a typical lot of 40 plugs. The leakage was measured by L. G. Sawyer, using the regular methods of the ignition staff of the Bureau. The following information will be of assistance in reading this table: Of the 12 broken plugs, 6 leaked badly and 6 did not leak at all; of those that leaked badly, 4 contained loose wires, and in the case of 1 of these the wire could be pulled out easily. It is evident that tests for gas leakage on new plugs give no indication of their gas leakage after use and that this leakage does not necessarily produce broken porcelains.

(*d*) SPARK PLUGS WITH MECHANICAL SEALS.—On account of the difficulties incident to the use of cement between the electrode wires and porcelains in spark plugs, the elimination of the cement and the use of a mechanical seal at the top of the porcelain is greatly to be desired. The mechanical stress incident to the use of such seals should be localized at the top of the plug. The type of porcelain developed by the Bureau in body No. 152 has sufficient strength to withstand the necessary stresses. At least two manufacturers of spark plugs are following the above suggestion of the Bureau and tests of spark plugs made in this manner have shown that this type of construction gives good serviceable spark plugs and that it offers possibilities of successful commercial development. The mechanical seals can be made in a variety of ways. The Bureau is interested in suggesting the type of construction. In this connection it may be noted that spark plugs with glass insulators are made without the use of cement. In this case the glass is sealed directly onto thin wire electrodes.

## V. SUMMARY

1. Of various typical cements for spark-plug electrodes made by mixing silicate of soda with different powdered solids, a mixture of raw kaolin with silicate of soda was found most satisfactory.

2. Chemical reactions take place either in the cold or on heating between silicate of soda and the solids commonly blended with it in making cements for spark-plug electrodes. With the exception of those occurring in blends of raw kaolin and silicate of soda, these reactions impair the utility of the mixtures for use as cements and promote the destruction of the electrode wires.

3. The practice of cementing electrode wires with high coefficient of thermal expansion into porcelains with low coefficients tends to produce cracked porcelains in spark plugs in use.

4. Gas leakage in moderate or large amounts was found in 90 per cent of a typical lot of used spark plugs in which the porcelain was not broken. It was evident that in these cases the cement failed instead of the porcelain and that gas leakage does not necessarily produce broken porcelains.

5. Preliminary tests indicate that it is possible to produce satisfactory spark plugs by the use of mechanical seals and thus to avoid the use of electrode cements with their attendant disadvantages.

WASHINGTON, August 22, 1919.

DEPARTMENT OF COMMERCE

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No. 156

# METALLOGRAPHIC FEATURES REVEALED BY THE DEEP ETCHING OF STEEL

BY

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# METALLOGRAPHIC FEATURES REVEALED BY THE DEEP ETHCING OF STEEL

By Henry S. Rawdon and Samuel Epstein

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Method | 4 |
| III. Features revealed by deep etching | 4 |
| 1. Chemical inhomogeneity | 4 |
| 2. Mechanical nonuniformity | 7 |
| 3. Physical discontinuities | 13 |
| IV. Nature of defects revealed in rails containing transverse fissures | 23 |
| V. Summary and conclusions | 23 |


## I. INTRODUCTION

The term "deep etching," as used here, refers to the use of acids of relatively high concentration for the roughening of the surface of metallographic specimens. Samples etched in this manner are intended primarily for a study of the macroscopic structure rather than for microscopic examination. In general, a very mild etching reagent is required for the latter purpose. The deep etching of steel is one of the earliest metallographic methods used for the study of iron and steel, particularly for a quick shop test. The method has, however, been given prominence recently by its application to the study of rails containing the defects known as transverse fissures and of steel forgings containing similar defects.[1]

Various views have been put forth as to the nature of the features revealed by this method of etching. The interpretations of the features revealed in transverse fissured rails by this method of etching may be cited as typical of the difference of opinion existing. That a variation in solubility of the steel in different directions is responsible for the transverse "cracks" revealed by the etching is one extreme view held. The other extreme is that

[1] F. M. Waring and K. E. Holaumann, The Deep Etching of Rails and Forgings, A. S. T. M. Proceedings, 19, 1919, also discussion on the same. H. M. Wicklhorst, Transverse Fissure Rails on Atchison, Topeka & Santa Fe R. R., heat 31155, report No. 56 to rail committee, Am. Ry. Eng. Assn., April, 1919. P. H. Dudley, Report on Transverse Fissures, report No. 55 to rail committee, Am. Ry. Eng. Assn., January, 1919. H. Baucke, Action of Electrol. tes upon Metals under Stress, Int. Zeit. für Metallographie, 4, p. 129, also Proc. Int. Assn. Test. Materials, VI[th] Congress, 1912.

cracks exist throughout the interior previously to the etching and that the etching merely renders them visible. According to still another view, the existence of internal stresses of a rather high magnitude may be responsible for the results produced. In order to show clearly the various conditions which this method of etching will reveal, together with the description of suitable methods for distinguishing between the different features, the series of examinations described below was undertaken.

## II. METHOD

Various acids have been used for the deep etching of steels. The different mixtures vary considerably from alcoholic hydrochloric acid (1 volume alcohol to 1 volume hydrochloric acid, specific gravity 1.19) used by Baucke [2] to a rather complex mixture of hydrochloric and sulphuric acids (9 volumes hydrochloric acid, 3 volumes sulphuric acid, 1 volume water) used by Waring and Hofammann.[3] In the work described below hydrochloric acid (specific gravity, 1.19) was used; this was heated nearly to 100° C before the specimens which had been previously ground smooth were immersed. This is the usual practice with all solutions other than the alcoholic ones. Heating, however, should not be regarded as a necessity—it merely hastens the action. Several other acids were tried to show their action upon materials known to be defective; these included nitric acid (1 volume of acid to 1 of water) and sulphuric acid similarly diluted. Both of these reagents revealed the defects, although the action was not so rapid as in the case of hydrochloric acid. The conclusion appears to be warranted that, provided the acid is concentrated enough to give a vigorous reaction, the choice of the acid to be used is a matter of minor importance.

## III. FEATURES REVEALED BY DEEP ETCHING

The different features which may be revealed by the deep etching of steel may be considered under the following headings: Chemical inhomogeneity, mechanical nonuniformity, and the presence of physical discontinuities within the steel.

### 1. CHEMICAL INHOMOGENEITY

The use of acid etching for the purpose of revealing variations in the distribution of the various chemical constituents which may occur in steel is so well known as to require only a brief

[2] Loc. cit. [3] Loc. cit.

discussion. The variations in the chemical composition are usually the direct result of the segregation accompanying solidification, although occasionally other factors may be responsible; for example, lack of complete solution and diffusion of the special additions in alloy steels, composition changes which may occur in such processes as welding, carburization, etc.

Figure 1 illustrates the case of chemical inhomogeneity due to segregation. The bar evidently has been rolled from an ingot having a decidedly segregated center; the difference in composition between center and outer portions has persisted throughout the process of rolling. The steel has the composition shown in Table 1.

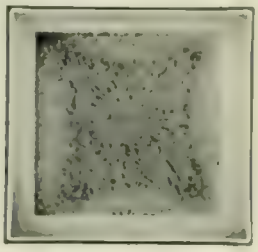


FIG. 1.—*Chemical inhomogeneity of rolled steel revealed by deep etching*

The highly segregated center of the ingot has persisted throughout the rolling of the material to the one-half-inch square shown. × 1

The greater solubility of the abundant sulphide streaks in the central portion as compared to the purer metal is responsible for the roughened appearance of the center. Each dark spot (Fig. 1) represents a pit which was previously occupied by sulphide or some other inclusion. These pits are later deepened and enlarged by the action of the acid after the inclosed impurity has been removed.

**TABLE 1.—Composition of Segregated Steels**

| Specimen | Carbon | Manganese | Phosphorus | Sulphur | Silicon |
|---|---|---|---|---|---|
| Segregated bar (Fig. 1): | Per cent | Per cent | Per cent | Per cent | Per cent |
| Outside layer | 0.08 | 0.45 | 0.076 | 0.029 | 0.002 |
| Segregated center | .09 | .45 | .138 | .064 | .002 |
| Steel casting (Fig. 2) | .31 | .75 | .039 | .053 | .263 |

Fig. 2 illustrates a condition which has resulted from what may be termed "secondary segregation." The photograph shows a section of a large steel casting which, although it met the prescribed specifications as to mechanical properties and heat treatment, fractured as a result of the handling received during transportation. The composition is given in Table 1. The macroscopic examination of the material after deep etching, together with the subsequent study of the microstructure, showed that although a sufficient grain refinement had been brought about by the annealing which the material had received (72 hours at 900° C (1650° F), cooled in furnace) the material still

FIG. 2.—*Chemical inhomogeneity of cast steel revealed by deep etching*

The specimen was photographed after being moistened with glycerin. Although the steel casting was annealed for 72 hours at 900° C, the original dendritic pattern persists. The distribution of the impurities, originally located in the angles between the dendrites, has not been changed by the treatment. ×½

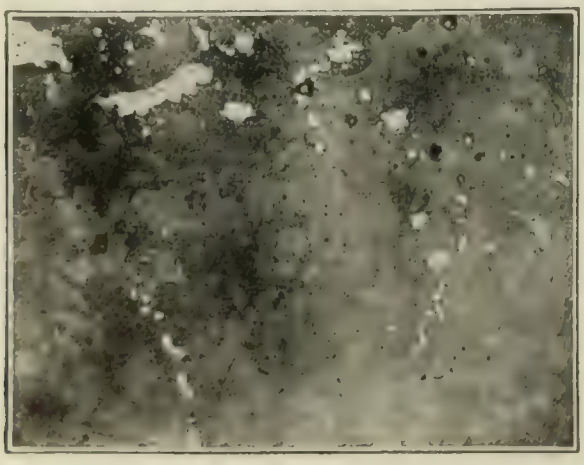


FIG. 3.—*Porous condition of cast steel*

Same material as Fig. 2, heat tinted. The white spots which are due to the exudation of alcohol and water used for washing from within the metal have prevented the uniform coloring of the surface. Each spot marks a porous area. ×5

possessed essentially the same dendritic structure that resulted upon casting. This was due to secondary segregation or the occurrence of numerous inclusions between the treelike crystals. Such impurities are not materially changed by heat treatment either in location or chemical composition and hence the original appearance, and many of the accompanying mechanical properties, are maintained in spite of the annealing. The microscopic examination showed also that in addition to the inclosures trapped between the fingers of the dendrites, the metal was also porous and spongy at such points. This is shown in Fig. 3. The specimen was polished and cleaned as for microscopic examination but was heat tinted to reveal the structure instead of being etched. The water and alcohol used for washing and drying the surface were absorbed at each porous spot and oozed out upon heating, thus preventing a uniform oxide tint from forming at such spots. The action of the deep etching upon the material shown in Fig. 2 has consisted essentially, then, in the relatively more rapid dissolving of the impurities and in the enlarging of the pores of the spongy areas. In addition to these features, Fig. 2 also illustrates what may be found in welded materials etched in this manner. The projection or boss in the upper portion of the figure was added after the main casting had been made. The white (deeply etched) line marks the junction surface between the two.

A special application of the use of deep etching in the inspection of wrought iron is illustrated by Figs. 4 and 5. Wrought iron, when ground smooth or filed and then etched with concentrated acid,[4] shows the presence of steel streaks by the white glistening appearance of such streaks; the body of the wrought iron remains dark. Fig. 4, *a*, shows the appearance of a large commercial wrought-iron shackle which was examined to determine its purity. The white streaks are of steel and have the structure shown by Fig. 4, *b*.

Fig. 5 shows the results of a similar examination of a bar of high-grade Swedish iron. The light streaks are of steel of a composition approaching that of eutectoid steel.

### 2. MECHANICAL NONUNIFORMITY

It is quite often the case that metals, even when subjected to no service load or stress, are far from being in a state of mechanical uniformity. Internal initial stresses of considerable magnitude

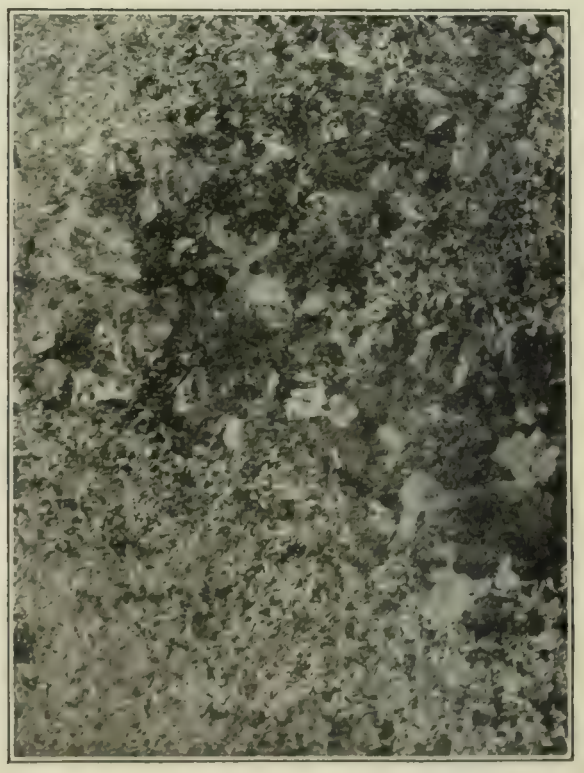
[4] Steel in Wrought Iron, Iron Age, 97: p. [illegible], 1916.

(*a*) Polished specimen of commercial wrought iron, deeply etched in concentrated hydrochloric acid. ×1

(*b*) Microstructure of one of the white bands of (*a*) above. The material of the bands has the structure of low carbon steel. Etching, 2 per cent alcoholic nitric acid. ×100

FIG. 4.—*Chemical inhomogeneity of commercial wrought iron revealed by deep etching*

(*a*) Polished specimen of Swedish wrought iron deeply etched in concentrated hydrochloric acid. ×1



(*b*) Microstructure of one of the white bands of (*a*). The material here has the structure of a steel of nearly eutectoid composition. Etching, 2 per cent alcoholic nitric acid. ×100

FIG. 5.—*Chemical inhomogeneity of high-grade Swedish wrought iron revealed by deep etching*

often exist, particularly if the material has been cold worked Very sudden or unequal cooling of different parts of the same piece may give rise to a similar condition. Considerable work has been done on this subject as related to brass and bronzes, and materials of this kind highly internally stressed may be made to crack spontaneously by the use of proper etching reagents.[5] As yet, but little attention [6] has been paid to the behavior of steels in this respect.

As suitable material for demonstrating the effect of deep etching by concentrated acid upon steels initially stressed internally, commercial balls for ball bearings of different sizes and grades were used. The chemical composition of the specimens used is given in Table 2.

**TABLE 2.—Chemical Composition of Balls Used**

| Diameter of ball | Carbon | Manganese | Phosphorus | Sulphur | Silicon | Chromium |
|---|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| 1 inch | 1.05 | 0.32 | 0.013 | 0.030 | 0.15 | 1.28 |
| ½ inch | .94 | .38 | .018 | .022 | .18 | (a) |
| ⅜ inch | 1.25 | 25 | .011 | .016 | .21 | .007 |

[a] Not detected

As shown in the above table, balls of three different sizes and compositions were used. The appearance of the balls after etching gave rather definite indications as to the method of manufacture. Some of the smallest balls had been turned out by lathe tools, as was clearly shown by the ends of the fibers on the opposite faces of the balls after etching. All of the others showed the two poles and work lines which are evidence of forging and pressing. The 1-inch balls most probably were forged individually; the others by the string method.

Previous to etching, the balls were examined for the presence of cracks or other surface defects by the magnetic method to be described later. None of the specimens was found to be defective. The behavior of the balls when etched with hot concentrated hydrochloric acid was determined for the material in the commercial state; that is, as received and also after different heat treatments. Some of the specimens were also sectioned in half, some perpendicular, and others parallel to the direction of the fibers. The results of the deep etching tests are summa

[5] B. S. Tech. Paper Nos. 82, 84, and 84. The technical literature of the subject is summarized in No. [illegible]
[6] Baucke, loc. cit.

TABLE 3.—Action of Deep Etching Upon Balls for Ball Bearings

A. COMMERCIAL BALLS

| Diameter | Weight (grams) | | Results |
|---|---|---|---|
| | Before etching | After etching | |
| 1 inch | 66.95 | 13.43 | Did not split. |
| | 66.93 | 24.75 | Do. |
| | 66.95 | 29.86 | Do. |
| ½ inch | 11.85 | 9.50 | Split through poles. |
| | 11.86 | 2.84 | Did not split. |
| | 11.86 | 7.15 | Split through poles. |
| | 11.86 | 9.17 | Do. |
| | 11.85 | 6.55 | Did not split. |
| | 11.86 | 9.34 | Split through poles. |
| | 11.87 | 2.97 | Did not split. |
| ¼ inch | 3.51 | 2.51 | Split through poles. |
| | 3.51 | 1.78 | Do. |
| | 3.51 | 2.02 | Do. |
| | 3.47 | .92 | Did not split. |
| | 3.48 | 1.32 | Do. |
| | 3.46 | 1.75 | Do. |
| | 3.49 | 1.83 | Do. |
| | 3.51 | 1.23 | Do. |

B. HEAT-TREATED BALLS (HEATED TO 900° C, COOLED IN AIR; HEATED TO 850° C QUENCHED IN COLD WATER (20° C))

| | | | |
|---|---|---|---|
| 1 inch | 65.86 | 43.68 | Did not split. |
| ½ inch | 11.73 | 7.65 | Split through poles. |
| | 11.45 | 11.35 | Do. |
| | 11.74 | 2.70 | Did not split. |
| ¼ inch | 3.39 | 1.70 | Do. |
| | 3.45 | 3.43 | Split through poles. |

C. HEAT TREATED (HEATED TO 900° C, COOLED IN AIR; HEATED TO 850° C, QUENCHED IN OIL)

| | | | |
|---|---|---|---|
| 1 inch | 65.75 | 49.5 | Did not split. |
| ½ inch | 11.74 | 4.45 | Do. |
| | 11.73 | 7.73 | Do. |
| | 11.73 | 3.3 | Do. |
| ¼ inch | 3.45 | 1.5 | Do. |
| | 3.42 | 3.25 | Do. |
| | 3.43 | 1.6 | Do. |

D. COMMERCIAL BALLS SECTIONED IN HALF

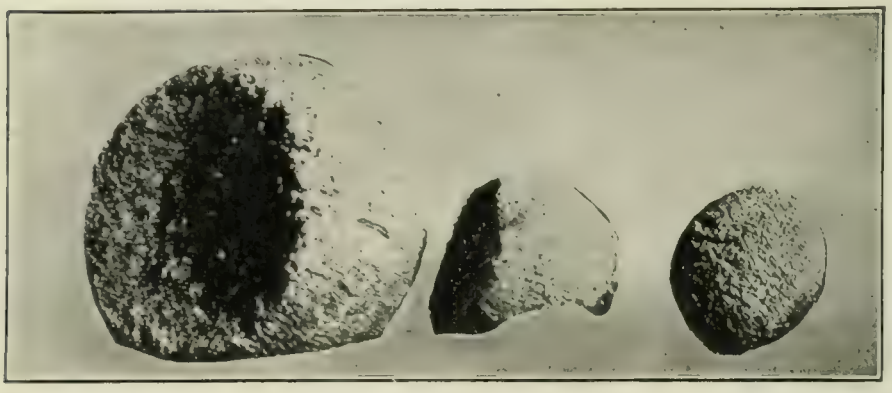
| | | | |
|---|---|---|---|
| 1 inch | 32.85 | 17.50 | Did not split. |
| | 47.72 | 35.50 | Do. |
| ½ inch | 7.45 | 3.85 | Do. |
| | 5.42 | 4.85 | Split through pole. |
| ¼ inch | 1.75 | .93 | Did not split. |
| | 2.33 | 1.35 | Do. |
| | 1.95 | .95 | Do. |
| | 1.93 | .80 | Do. |

rized in Table 3. Since it was necessary to remove the specimens from the acid at stated intervals for examination, the loss of weight rather than the length of the etching period has been given as being more indicative than the time of etching of the amount of etching necessary to demonstrate which balls are defective.

It will be noticed from the above table that none of the large (1-inch diameter) balls showed any tendency to split upon deep etching, as did over 50 per cent of the medium-sized (one-half-inch diameter) balls and about 30 per cent of the small (three-eighths inch diameter) ones. The small ones which split were limited entirely to those which, as shown by the appearance of the etched surface, had been forged (or pressed) rather than turned out.

Fig. 6, *a*, *b*, and *c*, shows the appearance of some of the balls after etching. The specimens were removed from the acid as soon as the cracks appeared, hence before the openings had been widened appreciably by the acid. In all cases the cracks are very definite ones, resembling knife cuts extending through the poles and often reaching in as far as the center of the ball. They follow somewhat the direction of the fibers of the material. Without doubt the splitting of the balls under the corrosive action of the concentrated acid is to be attributed to the presence of initial stresses of relatively high magnitude in the material. It was not possible, on account of the nature of the material, however, to attempt any measurement of the approximate value or distribution of such stresses. The sudden appearance of the cracks, the immediate widening of the fissure with an appreciable accompanying increase in the diameter of the ball, the occurrence of such cracks only in the forged or pressed material and in the smaller balls which had been hardened entirely throughout, the failure of all the materials to split when hardened less severely than the commercial material, and the definite orientation of the cracks with respect to the poles of the balls all are lines of evidence indicating the presence of internal stresses as the cause of the behavior of the balls upon deep etching. Baucke [7] in his discussion of experiments along this line states that it is necessary to section the balls before etching, and that whole balls etched intact will not split. In order to demonstrate whether the tendency of sectioned balls to split upon etching is greater than that of whole balls, a series of specimens were sectioned. The results

[7] Loc. cit.



(*a*) Fragments of three balls, respectively 1, one-half, and three-eighths inch in diameter, after prolonged etching in concentrated hydrochloric acid. These balls did not split. ×2

(*b*) Appearance of balls, one-half and three-eighths inch in diameter, which split when deeply etching, as a consequence of the initial stresses in the material. All of these balls were made by forging or pressing, as indicated by the definite poles. The cracks originate at the poles. ×2

(*c*) Appearance of balls, three-eighths inch in diameter, after etching. The two balls at the right were turned out, the other two were forged or pressed. None of the balls which were turned out could be cracked by deep etching. ×2

FIG. 6.—*Presence of initial stresses in hardened steel revealed by deep etching*

obtained upon etching are tabulated under D, Table 3. In general, the tendency to split upon etching appears to be less for the sectioned balls than for the whole ones. It is very probable that the stresses within the material are materially relieved by cutting the ball in two, and hence they would be expected to show less tendency to split in the acid.

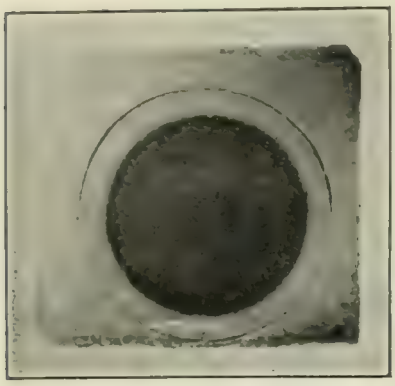
The method used for sectioning the hardened balls is of interest. A cylindrical hole very slightly smaller across than the diameter of the ball was drilled into a block of soft steel to a depth slightly greater than the radius. The ball was pressed into the hole by squeezing in a vise and the portion projecting beyond the face of the steel block was ground off on a wet grinding wheel. No evidence of tempering of the hardened balls during grinding could be observed in the polished specimen.

Fig. 7, *a*, *b*, *c*, and *d*, shows the structure of the large (1-inch diameter) balls. The outer metal has been rendered martensitic to the depth shown in Fig. 7, *a*. The central portion is largely troostitic. In Fig. 8 the structure typical of the small and the medium sized balls is shown.

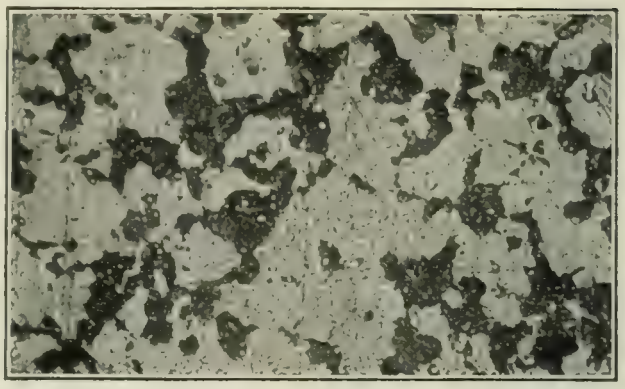
These specimens were martensitic throughout. This difference in microstructure is in accordance with the results of the etching tests—only the severely hardened specimens showed any tendency to split upon deep etching. It will be noted in Table 2 that the balls of one-half inch diameter are of a steel containing no alloying element and of a carbon content considerably lower than that of either of the other two. In order to render this steel relatively as hard as the other two types, a much more severe treatment must be resorted to, and this fact probably accounts largely for the greater tendency of this series to split than the other two. That the mechanical work which the material received (i. e., the magnitude of the internal stresses) also contributes to the tendency to split is evident in view of the fact that balls of similar size and hardness (i. e., as indicated by the structure) turned out in the lathe rather than forged or pressed showed no tendency to split upon etching.

### 3. PHYSICAL DISCONTINUITIES.

A third condition which may be revealed by deep etching is the presence of discontinuities within the steel. These may be in the form of pores or tiny cavities whereby the metal is rendered spongy, as previously described, or as separations or fissures, the two faces of which are often in such intimate contact that the

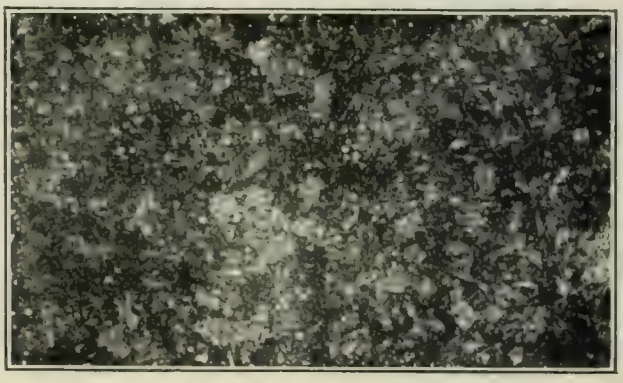


(*a*) Hardened ball, 1 inch in diameter, cut through the center and polished. ×1



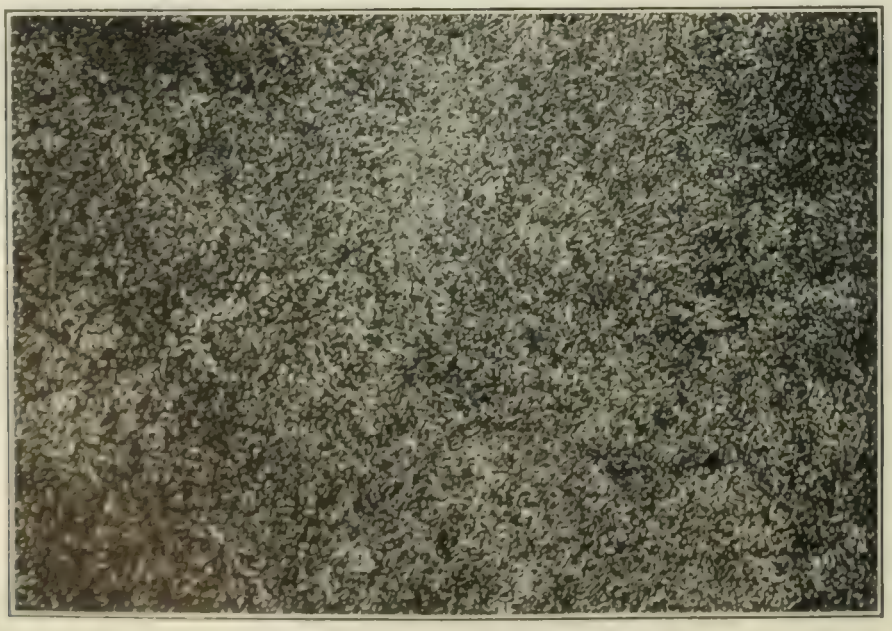
(*c*) Microstructure of the intermediate thin zone between the outer light-colored layer and the dark-colored central sphere of (*a*). This transition zone consists of martensite and troostite with some specks of carbide. ×500

(*b*) Microstructure of the outer spherical layer (light-colored) of (*a*). This layer is martensitic throughout with tiny globules of cementite. ×500



(*d*) Microstructure of the central sphere of (*a*). The metal is largely troostite with specks of carbide. None of the balls of this size split when deeply etched with concentrated acid. Etching, throughout, 2 per cent alcoholic nitric acid.

FIG. 7.—*Structure of hardened steel balls*



Microstructure of the balls one-half and three-eighths inch in diameter. These balls were martensitic throughout. This structure is typical of the specimens which split when deeply etched with acid. Etching, 2 per cent alcoholic nitric acid. ×500

FIG. 8.—*Microstructure of hardened steel balls*

defects can be definitely located only by special methods and with great care. Two types of materials characteristic of the second condition are flaky gun steel and rails containing transverse fissures.

In Fig. 9 is shown the appearance of a specimen of a defective gun forging (composition: Carbon 0.38 per cent, chromium 0.20 per cent, nickel 2.92 per cent) in which the defects are quite readily detected after polishing. Deep etching accentuates these by widening and deepening the fissures.

Fig. 9, *c*, shows the appearance of a section of a 1-inch round trepanned out of a large bloom of gun steel similar to that of the forging of Fig. 9, *a*, suspected of being defective. Subsequent deep etching revealed the cracks shown in Fig. 9, *c*. Presumably the cracks here revealed are identical with the defects found in the finished forging (Fig. 9, *a* and *b*). It will be noted that the crack is intercrystalline for the greater part of its course.

Defects similar in appearance to those just described have been found in abundance in rails containing transverse fissures, by means of deep etching.[8] In this case, however, the presence of the defects, gashes or cracks, in the material previous to etching has never been demonstrated. Hence there have resulted considerable differences of opinion as to the significance of the results obtained by the deep etching of transversely fissured rails. As materials typical of this type of defect, specimens were taken from three different rails which had developed transverse fissures in service. The compositions of the three, which differed widely in this respect, are listed in Table 4.

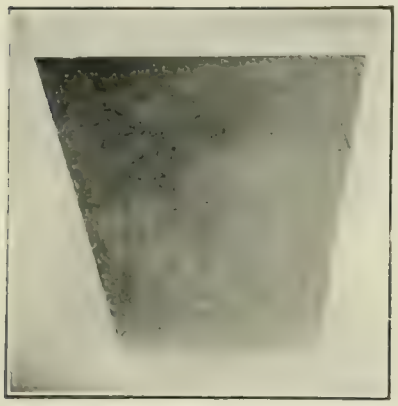
**TABLE 4. Composition of Rails Containing Transverse Fissures**

| Rail No. | Carbon | Manganese | Phosphorus | Sulphur | Silicon | Chromium | Nickel |
|---|---|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| 1 | 0.63 | 0.71 | 0.014 | 0.022 | 0.09 | 0.50 | 1.89 |
| 2 | .62 | .91 | .020 | .036 | .01 | [1] | [1] |
| 3 | .90 | 1.22 | .094 | [illegible] | .14 | [1] | [1] |

[1] Not detected.

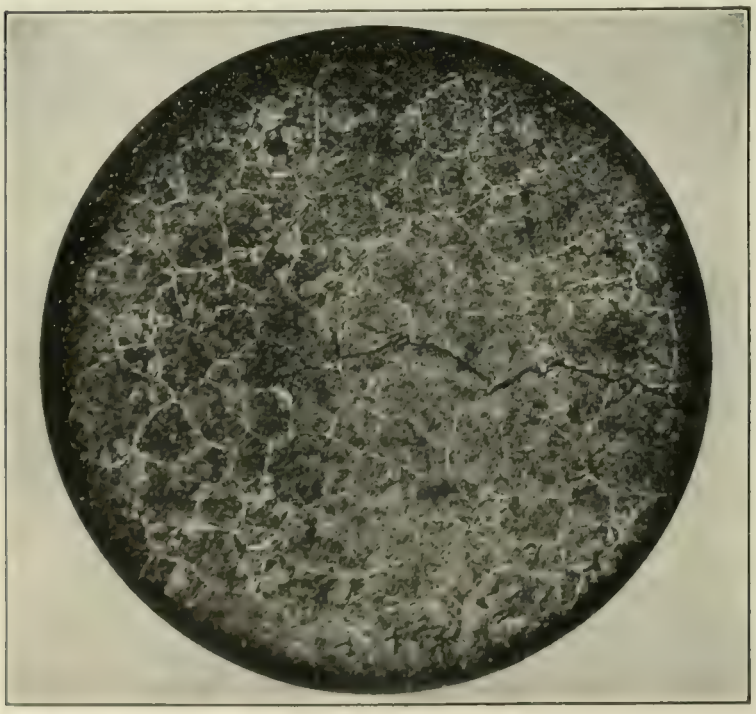
Portions of the head of each of the three rails were cut parallel to the tread into a series of slices. Each of the slices, after grinding, was etched to demonstrate the presence of gashes of transverse cracks. In each case these were found in abundance in the central

[8] Waring and Hofammann, loc. cit. Wickhorst, loc. cit.



(*a*) Transverse radial section from a forging for a gun tube polished to show interior defects. ×1

(*b*) Specimen (*a*) after deep etching in concentrated hydrochloric acid. The defects readily visible in (*a*) have been greatly widened and deepened by the etching. ×1



(*c*) Cross section of a 1-inch "round" trepanned out of a large bloom intended for a gun tube, etched with 2 per cent alcoholic nitric acid. The crack, which undoubtedly is of the same origin as the defects in (*a*) and (*b*), probably originated at a rather high temperature. It is largely intercrystalline in its course. ×3

FIG. 9.—*Defects in gun forgings revealed by deep etching*

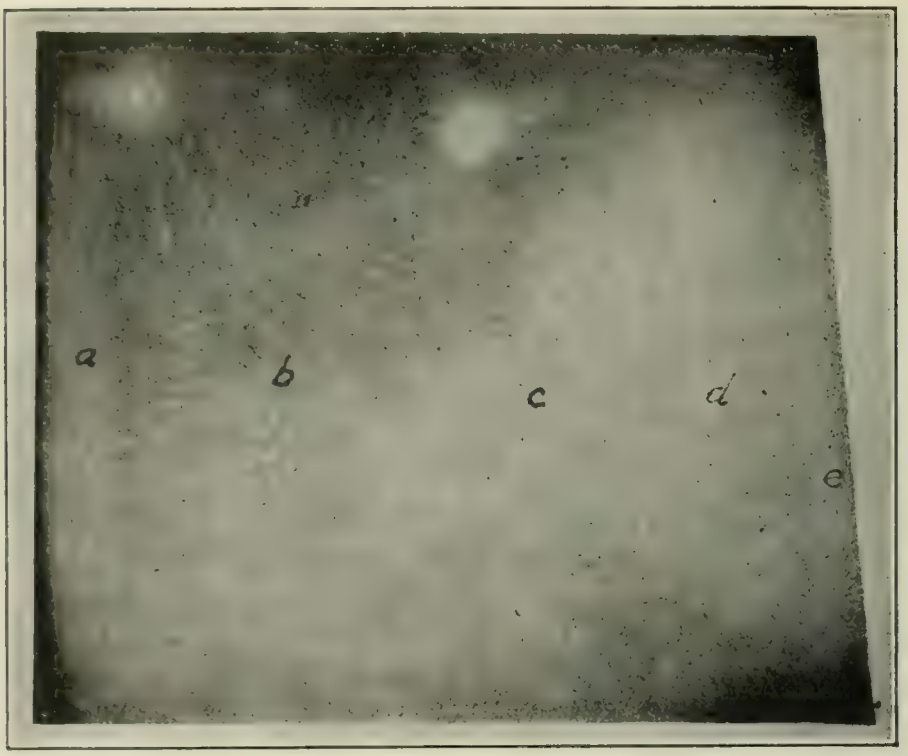
and lower portions of the head, as has been shown by previous investigators.

It is extremely difficult, however, to demonstrate by ordinary metallographic methods the presence of these defects within the material before the deep etching. Radiographic examination of thin slices (one-quarter inch thick) proved to be ineffective as a means for locating them. The only method by which the cracks could be located, without etching the specimen, was a magnetic one. This method was finally adopted for the preliminary examination of all the specimens suspected of containing cracks of any kind. The sample, which must be well polished, as for microscopic examination, is magnetized and then immersed in kerosene, or a similar liquid, containing *very* fine iron dust in suspension. "Cast-iron mud" from disks used for lapping was used for the purpose. The particles of iron dust collect upon the face of the specimen, and at the points where, because of a discontinuity in the metal, a change in the density of the magnetic flux occurs, orient themselves to correspond to the shape of the discontinuity. The specimens are then washed in clean kerosene to remove as much as possible of the excess iron dust which clings to the surface.[9]

In Fig. 10 is shown the appearance of a slice from the lower part of the head of the rail No. 3, which has been treated with the iron dust after magnetizing and the same specimen after deep etching. It is extremely difficult to photograph the specimen so as to clearly show the results of the treatment with iron dust. They are much more readily seen upon visual examination than might be inferred from the photograph. Comparison of Fig. 10, *a* and *b*, however, shows the presence of a very fine crack or discontinuity in the unetched specimen (Fig. 10, *a*) corresponding to each of those revealed by deep etching (Fig. 10, *b*).

The appearance of the cracks located by the magnetic method is more clearly shown in Fig. 11, somewhat magnified, in which the surface was viewed obliquely. Crack *b* (Fig. 10, *a*) was located by means of iron dust after magnetizing the specimen. Its position was then recorded by punch marks at each end of the crack. Fig. 11, *b*, shows the specimen after the iron dust was wiped off; no crack can be detected between the punch marks. Fig. 11, *c*, shows the same specimen after a second treatment with iron dust.

[9] This method for the examination of polished surfaces suspected of containing surface cracks was developed at the Bureau for the inspection of precision gages.




(*a*) Longitudinal section of the head of rail No. 3 (Table 4) parallel to the tread. The specimen was magnetized and then immersed in kerosene in which iron dust was suspended. The cracks indicated by *a*, *b*, *c*, *d*, and *e* were located

(*b*) Same specimen as (*a*) deeply etched with concentrated hydrochloric acid. The cracks revealed by deep etching correspond with those in (*a*). ×1

FIG. [illegible]—*Defects in rails containing transverse fissures revealed by deep etching*

Although it is known with certainty that a discontinuity exists in the metal between the two punch marks, it is extremely difficult to find evidence of it in the microstructure even after light etching. In Fig. 12 is shown the best indication found of the presence of such a crack. This is very faint, however, and would be disregarded in the ordinary microscopic examination as of little or no importance. The faces on the opposite sides of the discontinuity or fissure are in such intimate contact that even at a magnification of 500 diameters the crack is relatively very inconspicuous, as is shown in Fig. 13. The course of the crack which has been indicated by arrows is hardly more conspicuous than the dark boundaries of the pearlite masses.

In Fig. 14 is shown a slice cut from the head of rail No. 1, parallel to the tread, in which two defects have been located by

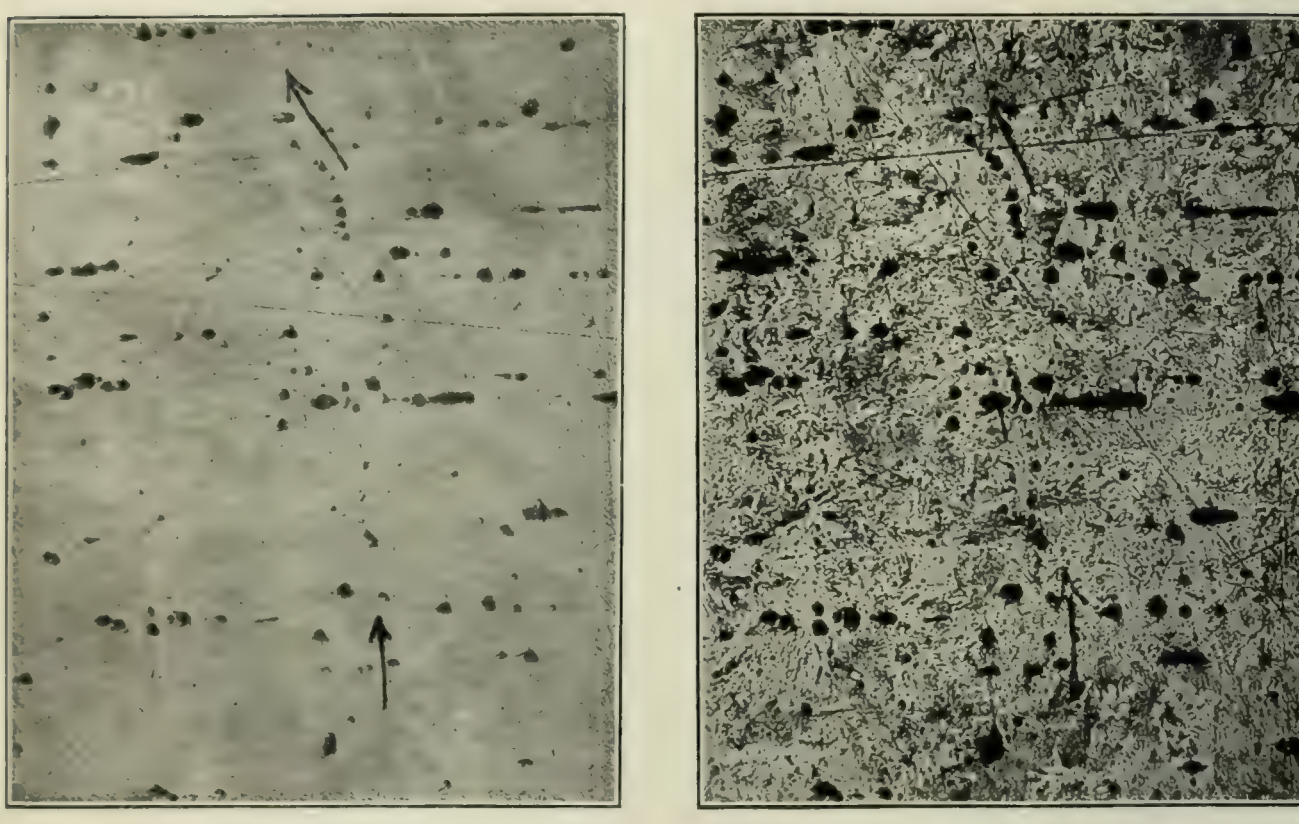
(*a*) (*b*) (*c*)

(*a*) Crack (*b*) of Fig. 10, *a*, viewed obliquely. ×3
(*b*) Same specimen as (*a*). The line of the crack shown in (*a*) was located by a punch mark at each end of the crack and the iron dust wiped off. No crack is visible ×3
(*c*) Same specimen as (*b*), treated a second time with iron dust. Compare with (*b*) ×3

FIG. 11.—*Interior cracks existing in rails of the transverse-fissure type.*

means of iron dust after magnetization of the specimen. By means of punch marks *close* to the ends of the crack it was found possible to open the fissure as is shown in Fig. 14, *b* and *c*. The slice containing the defects was then cut as shown by the lines in Fig. 14, *a*, and each strip broken transversely along the line of the defect. The break was localized by means of a slight saw cut on each side in line with the crack. The appearance of the fracture is shown in Fig. 14, *d*. A definite area which is easily distinguished from the surrounding sound material corresponds to the defect previously located. The strip containing crack *b* showed a similar characteristic spot when broken. This area, semicircular in Fig. 14, *d*, is identical in appearance with the nucleus of transverse fissures and with the gray spots often revealed in the transverse breaks of the heads of defective rails of this kind.

The nature of these defects can best be studied in material in which the carbon content is low enough so that the grain boundaries are clearly outlined by ferrite envelopes. Rail No. 2 was found



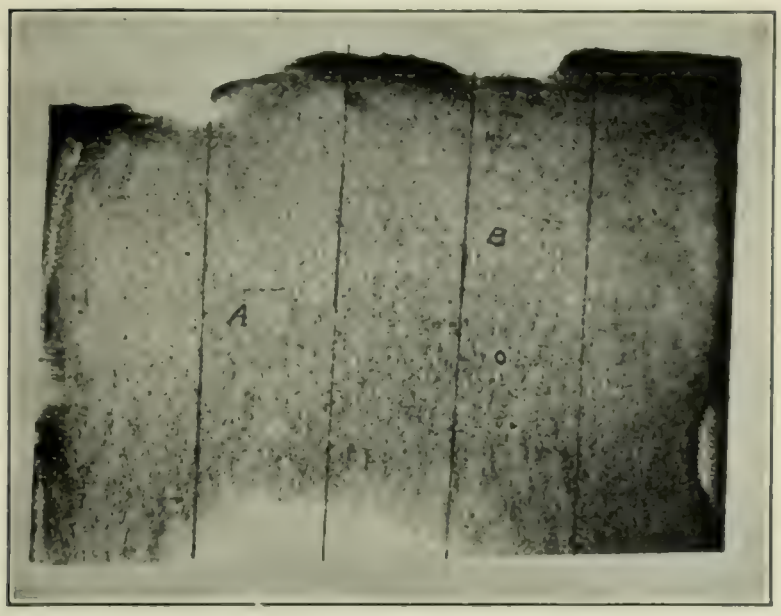
(*a*) (*b*)

FIG. 12.—*Microscopic appearance of cracks existing in rails of the transverse-fissure type*

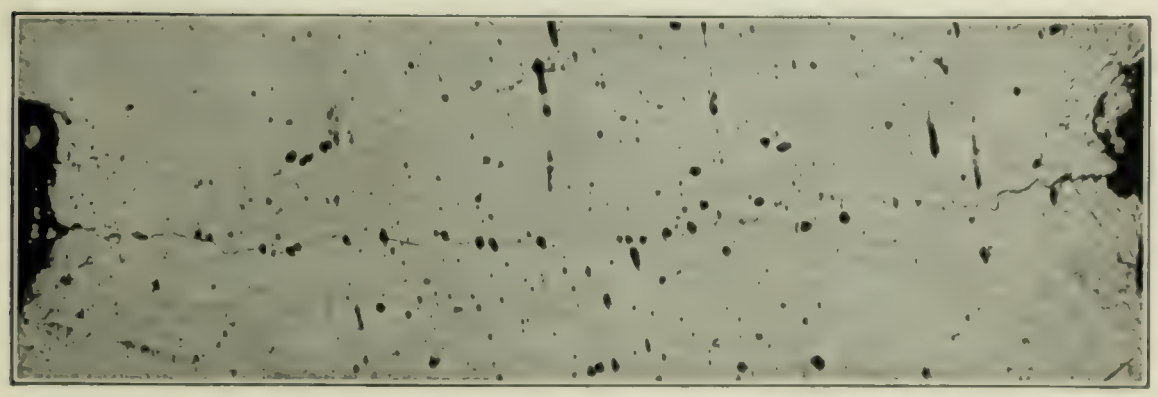
(*a*) Crack (*b*) of Fig. 10, *a*, specimen is unetched. ×50
(*b*) Same specimen as (*a*), etched with 2 per cent alcoholic nitric acid. The metal is in such intimate contact that only a very faint indication of the presence of the crack could be obtained. ×50

FIG. 13.—*Microscopic appearance of interior cracks existing in defective rails*

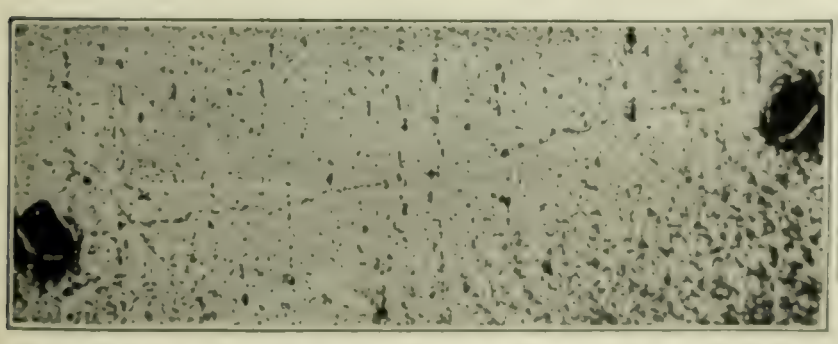
Crack (*b*) of Fig. 12, *a*, is shown after etching. ×500. The two sides of the crack are in such intimate contact that even at this magnification the course of the cracks (indicated by arrows) is relatively very inconspicuous.



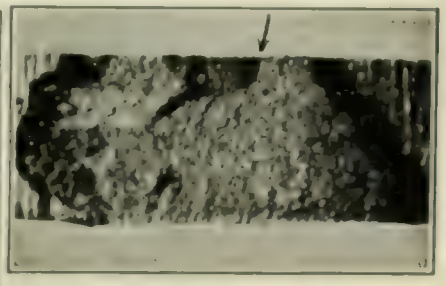

(*a*) Longitudinal section of rail No. 1 (Table 4) parallel to the tread. The two defects *A* and *B* were located by the magnetic method. ×1



(*b*) Defect *A* of (*a*) above. By means of a punch mark at each end the crack has been opened; specimen is unetched. ×50

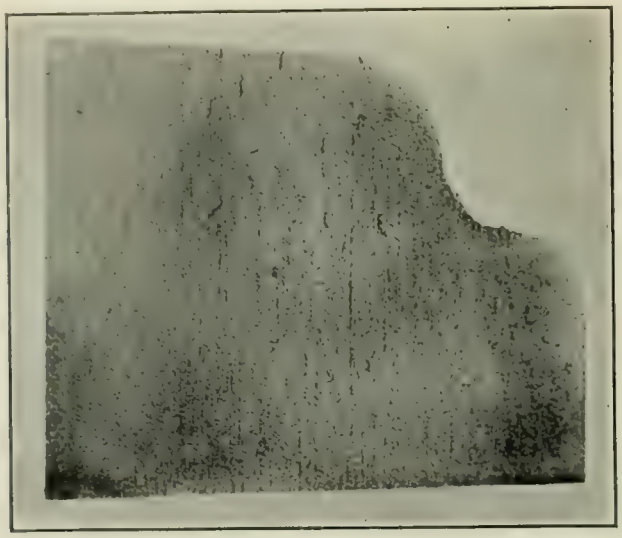


(*c*) Defect *B* of (*a*) above. The crack has been opened by means of punch marks as shown. Specimen was slightly etched with 2 per cent alcoholic nitric acid. ×10

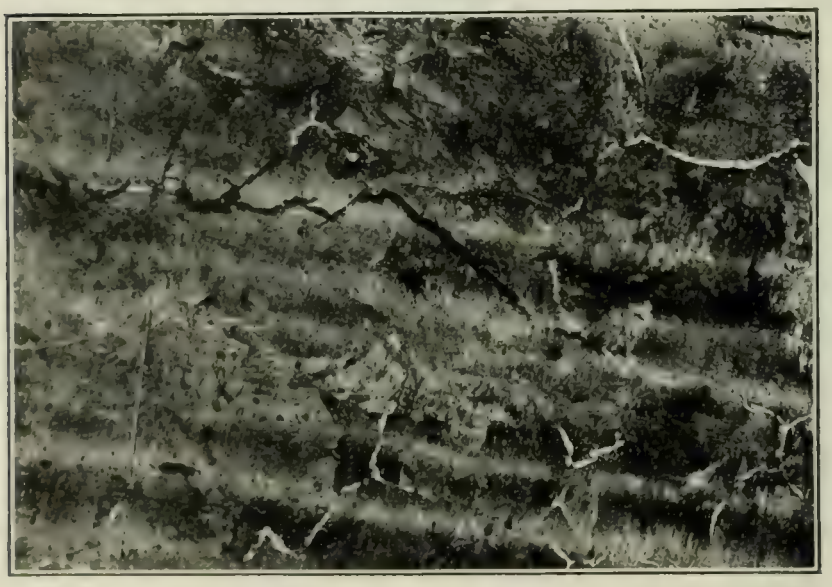


(*d*) Fracture of the strip of specimen (*a*) containing defect *A*. The rail section was cut into strips as shown, and fractured by a transverse break along the line of the defect. The semicircular area, indicated by the arrow, corresponds to the defect.

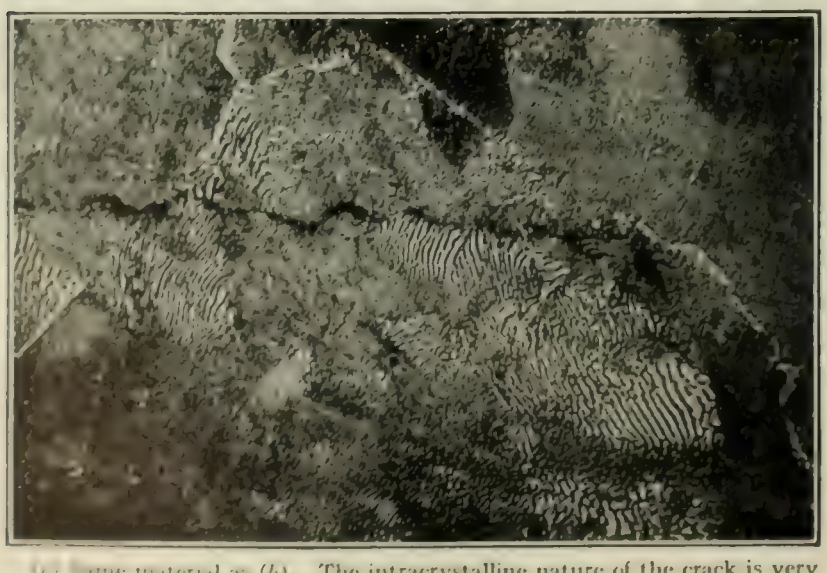
FIG. 14.—*Nature of the interior defects revealed by the deep etching rails containing transverse fissures*



(*a*) Longitudical section of rail No. 2 (Table 4) parallel to the tread. The interior cracks as they appear after slight etching with concentrated hydrochloric acid. ×1



(*b*) Specimen (*a*) after slight etching in concentrated hydrochloric acid to widen the crack, repolished for microscopic examination. The crack is intracrystalline in its course. There is some evidence of banding due to phosphorus. Etching, 2 per cent alcoholic nitric acid. ×100.



(*c*) Same material as (*b*). The intracrystalline nature of the crack is very evident. Etching, 2 per cent alcoholic nitric acid. ×500

FIG. 15.—*Microscopic nature of the interior defects found in rails of the transverse-fissure type*

to be very suitable for this purpose. Fig. 15, *a*, shows a section of this rail after slight etching with concentrated hydrochloric acid. The interior cracks having been widened by the concentrated acid, the surface was ground down, repolished, and reetched for microscopic examination. In Fig. 15, *b* (×100), and Fig. 15, *c* (×500), a crack is shown passing through the grains and across the grain boundaries. The cracks are intracrystalline, in their course; that is, the break has occurred *through* the grains rather than *between* them.

## IV. NATURE OF DEFECTS REVEALED IN RAILS CONTAINING TRANSVERSE FISSURES

The results of the examination given above definitely warrant the conclusion that the defects (gashes, fissures, or cracks), revealed in rails of the transverse fissure type by means of deep etching, exist within the material previously to the etching, as discontinuities within the steel. The function of the acid used for etching is merely to widen and deepen the *preexisting* cracks. The microscopic appearance of these cracks offers some suggestions as to their origin. The course of the crack is intracrystalline and has the general appearance of a fracture produced in normal material; there is no evidence of inherent weakness at the grain boundaries. An answer to the question as to whether the separation occurred while the metal was cold—that is, in the track—or while hot—that is, in the mill—does not appear to be forthcoming from the evidence offered by the examination of the fractures alone. No definite statement can be made on this point. However, the comparison of internal fractures found in ingots and blooms and hence, in all probability, produced at a rather high temperature (Fig. 9, *c*) with those found in rails which developed transverse fissures in service (Fig. 15) is very suggestive. The internal cracks shown in Fig. 9, *c*, are of the *inter*crystalline type. In general, this is a characteristic of fractures produced in metals at elevated temperatures. On the other hand, the cracks shown in Fig. 15 are of the *intra*crystalline type, a feature which, in general, is characteristic of fractures produced in metals broken at ordinary temperatures.

## V. SUMMARY AND CONCLUSIONS

1. The method of deep etching of steel by means of concentrated acids was examined in detail. The choice of the acid is a matter

of minor consideration provided it is concentrated enough to produce a vigorous attack of the metal.

2. The metallographic features of steel revealed by deep etching are of three general types: Chemical inhomogeneity, mechanical nonuniformity, and physical discontinuities.

3. Chemical inhomogeneity, usually the result of segregation, shows itself by a more vigorous roughening and pitting of the "impure" portions. Sulphides and other inclosures are rapidly dissolved and the resulting pits are then deepened and widened.

4. Steel which is not mechanically uniform throughout because of the presence of initial stresses, which may be the result of previous mechanical work or of too vigorous quenching during heat treatment, will split when deeply etched, provided the stresses are of sufficient magnitude. Commercial bearing balls of different types were used to illustrate this feature. It was shown that this tendency to crack upon etching may be eliminated by suitable heat treatment. The behavior of steel, in this respect, is identical with the corrosion cracking of brasses and bronzes.

5. Physical discontinuities, such as internal fractures, etc., which may exist in steel, are revealed by deep etching. The acid serves to widen and deepen these discontinuities within the metal.

6. It has been definitely shown that the gash defects found in abundance in rails in which transverse fissures have developed and in similar materials, are physical discontinuities or internal fractures which exist within the material previously to etching. The etching merely reveals the defect. A magnetic method for locating such defects in the unetched specimens is described. This method appears to be the only one for determining the nature of these and similar defects with certainty.

The authors are indebted to Maj. W. E. Hoke, under whose direction the magnetic method described was developed for the inspection of the surfaces of precision gages, and to F. H. Tucker, for the chemical analyses of the materials used.

WASHINGTON, September 20, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 157

# AN INVESTIGATION OF THE PHYSICAL PROPERTIES OF DENTAL MATERIALS

BY

WILMER H. SOUDER, Associate Physicist
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*Bureau of Standards*

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# AN INVESTIGATION OF THE PHYSICAL PROPERTIES OF DENTAL MATERIALS

By Wilmer H. Souder and Chauncey G. Peters

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| 1. Historical | 4 |
| II. Instruments | 5 |
| 1. The Black micrometer and Wedelstaedt tube | 5 |
| 2. The Black dynamometer | 6 |
| 3. The flow attachment | 7 |
| 4. Optical micrometers and comparators | 7 |
| III. Manipulation of alloy | 8 |
| IV. Dimensional changes with temperature | 9 |
| 1. Apparatus and methods | 9 |
| 2. Experimental procedure | 15 |
| 3. Results | 16 |
| V. Dimensional changes with time | 20 |
| 1. Apparatus | 20 |
| 2. Experimental procedure | 21 |
| 3. Results | 21 |
| VI. Flow under compression | 30 |
| VII. Crushing strength | 34 |
| VIII. Blackening of hand | 35 |
| IX. Chemical composition | 35 |
| X. Electrode-potential determinations | 37 |
| XI. Summary | 39 |


## I. INTRODUCTION

A recent request from a branch of the Government, purchasing large quantities of dental supplies, resulted in the authors taking up a systematic study of the physical properties of certain filling materials together with the instruments generally used in testing the same.

Properties, such as crushing strength, flow, thermal and chemical expansions, chemical composition, electrode-potentials and thermal reactions have been investigated. Additional phases, such as method of manipulation, time, temperature, etc., were found to exert definite influences in certain tests and indicated the necessity for their proper control.

It is believed that the discoveries in instruments will be of sufficient importance to justify lengthy descriptions since it was found necessary to discard practically all devices described in the dental text books. In the selection of instruments we have considered two features, viz, accuracy and simplicity.

Some of the alloys included in this research were made to requested specifications, others were purchased in the open market, and many were submitted by manufacturers cooperating in the investigation.

Many of the results should be interpreted as comparative or relative tests. Since it is not our purpose to advertise the merits or demerits of any material, the manufacturer's names have been omitted. Each has, however, been informed of the results found for his alloy. The purpose of this paper, as in all previous reports, is to place before those familiar with the use of dental materials accurate and reliable data, together with a description of instruments suitable for measuring the properties investigated.

We have attempted to discuss some of our results on a purely physical basis. Their clinical interpretation is left to those experienced in the profession.

It is hoped that at a near date and with the cooperation of the manufacturers and users of these materials it will be possible to write definite and proper specifications, which will enable the purchaser and user to secure articles of known qualities.

## 1. HISTORICAL

It is practically impossible to give a complete bibliography of the researches on amalgam during its 75 years of existence.

The first amalgams were manipulated in a crude and empirical way, thus entailing an unusually large number of failures. In fact, the feeling against amalgam was so strong at one time that any one speaking favorably of its possibilities was immediately boycotted by the profession. Is it any wonder that failures were very conspicuous when we read of the crude practices and lack of definite data on the manufacture and manipulation of alloys? Opinions and speculations seem to have been considered of more importance than data or accurate statistics.

Despite the failures the few successful restorations were so completely satisfactory that investigators started a search to find the essential properties and technique incident to satisfactory restorations. The works of the pioneers, Tomes, Fletcher, Hitch-

cock, Witzel, and Flagg, have been reviewed and elaborated by Black, who has probably done most to point out the necessity for accurate scientific tests. The chapter on amalgams in Volume II of Black's Operative Dentistry (1914) contains a world of information on early work, together with the results of his own extensive researches.

More recent laboratory researches are recorded in the various dental journals under the authorship of Marcus L. Ward, dean, U. of M. Dental School; A. W. Gray, research director, L. D. Caulk Co.; W. G. Crandal, Spencer, Iowa; C. M. McCauley, Abilene, Tex.; William E. Harper, Chicago, Ill.; A. Fenchel, Hamburg, Germany; B. R. Bakker, Utrecht, Holland; and McBain & Joyner, Bristol, England.

The findings of these men are not concordant in all essentials and the lack of definite descriptions of instruments and manipulative details makes it difficult to explain all the results reported. It is hoped that the present article may clear up some of the points in question among the various investigators and also enable those interested in continuing the work to proceed with apparatus of unquestionable accuracy and simplicity.

## II. INSTRUMENTS

The first instruments of importance for systematically testing amalgams were those of Dr. Black's design—the micrometer and dynamometer. These were of the utmost value in securing qualitative information and started a new era in amalgam manufacture, but they can scarcely be relied upon to give the most precise or decisive data. Few, if any, investigators are using them to-day. The writers are familiar with the apparatus used by Gray at Milford and by Ward at Michigan and feel sure that both types are an advance over the original apparatus of Black and quite accurate for their researches.

### 1. THE BLACK MICROMETER AND WEDELSTAEDT TUBES

Fundamental errors precluding the use of the Black micrometer for precision work are the mechanical impossibilities (to date) of combining a system of levers and gears to operate a dial or mirror indicator which will accurately or consistently measure directly to $\frac{1}{10\ 000}$ inch (2½ microns). Scale divisions on an instrument are not always an indication of its approximate sensitivity, although

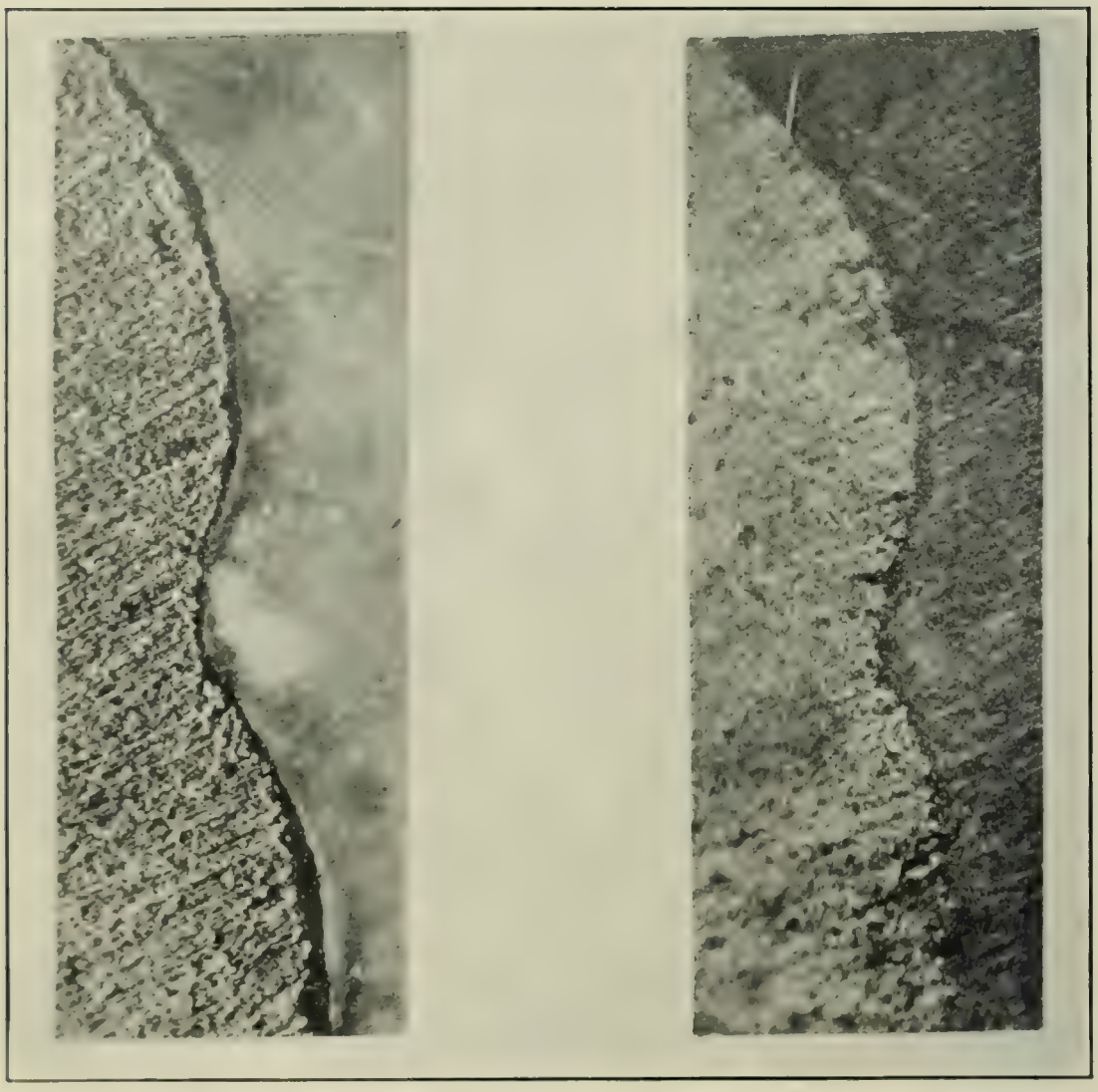
they should be. The elements of variance, passivity, and backlash always enter where there is a multiplicity of moving parts. These features, as affecting instrument design, are fully treated in an article by F. J. Schlink, Scientific Paper No. 328 of this Bureau.

The Wedelstaedt tubes used with this micrometer are subject to criticism because of their restraining action on the amalgam specimen. Later it will be seen that, as shown below, the expansion of amalgam is about two and one-half times as large as steel; hence on the least temperature rise the amalgam is frictionally locked against the sides of the tube and in many cases the excess expansion causes a bulging or "spheroiding" of its free surface. The same phenomenon will occur with chemical or crystallization expansions. Any later temperature drop will be accompanied by the larger contraction of the amalgam (see section on thermal expansion), thus giving the "black-ditch" effect. A slight heating of one of these tubes of amalgam is sufficient to cause an apparent excessive expansion or spheroiding followed by the ditch effect.

Again the "points" expansion are not in the same units as "points" contraction, since in the latter case the amalgam may shrink in all dimensions; whereas in the former the three dimensions of expansion have been forced into a threefold one dimension of expansion, two of which are now manifest as flow, but recorded as expansion. This probably accounts for the claim of slight expansion and no contraction which is often made for alloys; whereas in fact there is contraction which is too small for detection with such apparatus.

### 2. THE BLACK DYNAMOMETER

Little need be said about the dynamometer except that the results are of necessity irregular, due to the smallness of specimens. This smallness of specimen permits undue influence from slight variations of manipulation, mixing, or packing. Cubical forms are not well suited for these crushing tests. The exposed corners and equal dimensions are factors which should be avoided. For the proper test of compressibility, as outlined by the American Society for Testing Materials, specimens should be prepared in cylindrical form, 1 inch in diameter and 2½ to 4 inches long. Special attention is directed to the necessity of using specimens with a length greater than the diameter in order to avoid the "barrel" effect in case there is a tendency toward flow.



*a* *b*

Photo by R. E. Lofton, mag. × 55

FIG. 1.—*Amalgam-enamel margin*

Same margin viewed by different illuminations. Wrong interpretations often result from an improper use of the microscope

### 3. THE FLOW ATTACHMENT

Some types of dynamometers are equipped with an auxiliary flow dial which records the motion of the compression rod as the pressure is applied for crushing. The objections offered above apply equally well against this attachment as an instrument of precision.

The sudden shock given the levers and dial parts at the instant of rupture is sufficient to disturb the bearing surfaces and adjustments of all parts of the instrument.

### 4. OPTICAL MICROMETERS AND COMPARATORS

Unless handled by a person skilled in their use these instruments are of little value. The accompanying figure is included to explain the error possibilities of devices depending upon microscopes; (*a*) and (*b*), Fig. 1, are photographs of the same tooth, with absolutely no changes of position of microscope or tooth, the only change being a slight modification of the illumination. In the first instance there is no question about the imperfect adaptation of amalgam to tooth; in the second it appears reasonably perfect. The differences are even more striking when using the binocular microscope.

Micrometer microscopes are often used in comparing and calibrating line (length) standards. These, when arranged for the best possible accuracy—that is, best illumination and most suitable lines on a properly surfaced background—will give results agreeing within 1 micron. However, if only a single microscope is used and the displacement measured in terms of the run of a screw, settings having been made with the assistance of a microscope, then it is necessary to add to the uncertainties of the microscopic setting the errors and irregularities of the screw. A third source of error lies in the necessity of using an auxiliary contact to transmit any motion of the amalgam, since the new amalgam surface is constantly changing its character and necessarily also the character or appearance of any line or mark which may have been placed thereon.

The combined errors make it difficult, if not impossible, to detect variations of 1 or 2 microns, and again the slight contractions of samples in Wedelstaedt tubes may pass unnoticed.

Optical lever devices read by the mirror and scale method are only slightly, if any, better. Their use necessitates a multiplicity of contacts and bearing surfaces, each of which is subject to its

own peculiar action, and each introduces its inherent source of error.

The safer way to proceed in using any of the above instruments is to use samples of amalgam of larger dimensions, thus magnifying the effect and consequently increasing the accuracy of values.

Probably the best instrument for rough measurements is an ordinary small screw machinist micrometer adjusted for a specimen about 50 mm long. This instrument is reliable to better than $\frac{1}{200}$ mm ($\frac{1}{5000}$ inch), about 2 so-called Black points; but the specimen being about six times as long as the Wedelstaedt specimen there results a net increase in theoretical accuracy. Such an outfit properly handled in a thermostated chamber will be of more decisive value than many of the above-described instruments, which are used in looking for ditches or bulges and depend entirely upon the magnification of margins.

## III. MANIPULATION OF ALLOY

This subject is often lost sight of in the discussion of physical properties. Probably no other phase of the restoration is subject to greater carelessness. The dentist may spend unusual care in shaping the cavity after having removed a generous amount of good tooth structure to make sure the last traces of decay have been eliminated and then proceed to make up the amalgam on the assumption that the only requirement is to daub up the cavity. Or if the assistant is doing the amalgamation and starts too soon, he is instructed to keep working the mass until the cavity is ready. Another practice is to keep the mass plastic by the addition of slight amounts of mercury at intervals, thus making it possible to condense several cavities from the same mix. The serious effects of this over trituration will be found in another section.

The amalgamation and condensation procedure throughout this research (unless otherwise specified) was according to manufacturers' instructions. In the absence of definite instructions the following technique was adopted and is not seriously different from the majority of manufacturers' instructions.

The alloy and mercury were weighed in an approximate ratio, such that there would be a very slight excess of mercury on condensation. These were mixed (not ground) in a mortar for one minute. The amalgamated mass was then transferred to the hand and mulled two minutes. Part of the excess mercury was removed through chamois cloth. The artificial or matrix cavities were holes in steel blocks drilled and polished. The amalgam was

condensed in these, using three or four different-sized pluggers. Those specimens which failed to show perfect adaptation to the form were rejected. Sufficient alloy was used so that an excess of amalgam could be built up over the top of the cavity, and on tapping lightly it was usually possible to cause additional mercury to rise from the cavity. This excess mercury and amalgam was later removed and the specimen taken from the matrix. The condensation was usually completed in two or three minutes, depending upon the size and shape of specimen.

The slight excess of mercury used appeared to give the condensed amalgam a greater uniformity and prevent the formation of layers, when added quantities of amalgam were condensed in the cavity. These layers are fostered by delay in condensing, hence the desirability of using shorter times.

The greatest variation in results, when using a given manipulation, appears to arise not so much from slight irregularities in manipulation of alloy as from variation in alloy from package to package. All values reported for alloy *G*[1] are for the same package; this is also true for alloy I. A fair degree of agreement will be found for check tests on these alloys recorded in Table 3. Another method of securing uniformity of results resorted to by some investigators consists in packing specimens under continued mechanical pressure, allowing several minutes to elapse before removing them from the matrix. The authors have been more interested in finding what happens to amalgams as they are ordinarily used, or should be used, and have made an attempt to start tests early enough to discover all changes accompanying the reaction, regardless of variations.

## IV. DIMENSIONAL CHANGES WITH TEMPERATURE

### 1. APPARATUS AND METHODS

For the measurement of the thermal expansion of small samples, methods and apparatus which make use of the interference of light waves have been employed at this Bureau for several years. For some of this work the old-established Fizeau[2] method was used. Fig. 3 shows an interferometer devised by Priest[3] for determining the thermal expansion of single small pins. With

[1] Letters have been assigned to the trade names of the alloys and throughout this paper the same letter refers to the same alloy, but not necessarily to the same package of alloy except in the cases mentioned above.

[2] Fizeau, Annal de Chem. et al Phy. (4) 2. 143; 1863.

[3] Priest, B. S. Scientific Paper No. 365, 1920.

another form of apparatus, recently described by one of the authors,[4] the expansion of three different pins can be simultaneously determined. These interferometers have been thoroughly tried out and found to measure small displacements with an error of about 0.005 micron or 0.0000002 inch. Because of the extreme accuracy and directness of the method and the necessity of using small samples, the interferometer was used for the determinations of thermal expansion of teeth and dental materials. A rather complete description of the apparatus has been given here for those who may be interested in making measurements of this kind.

The interferometer is usually thought of as an extremely complicated apparatus, while in reality the essential parts are two

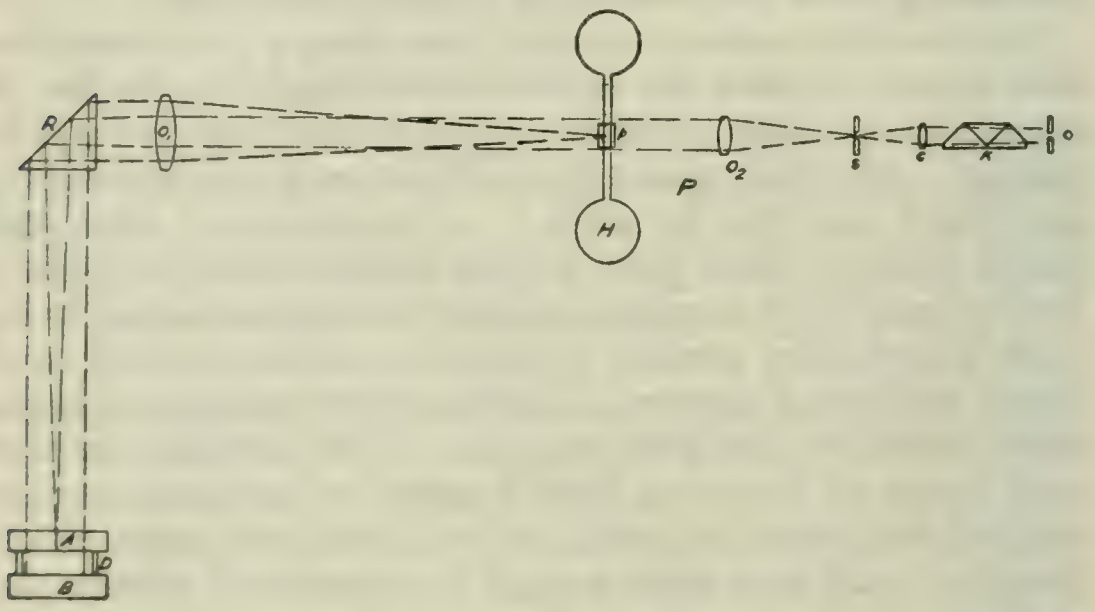



FIG. 2.—*Vertical section of apparatus*

plane glass plates which are held apart by a suitable separator. Fig. 2 shows a vertical section of the apparatus.

The two plates $A$ and $B$ and the ring $D$ constitute the interferometer, while $P$ represents a Pulfrich apparatus for viewing the fringes.

The light from a helium lamp $H$ is focused upon a small total reflection prism $p$. After being collimated by the lens $O_1$, it is reflected by the prism $R$ down to the interferometer plates $A$ and $B$ which are in the focal plane of $O_1$. The rays returning from points in the plane of the mirrors are collimated by the lens $O_1$, and an image of the interference pattern and the reference marks on the plates is formed by the lens $O_2$ upon the slit $S$ and viewed

[4] Peters, Jour. Wash. Acad. of Sci., 9, p. 281; 1919.

with the eye piece *C*. The direct vision prism *K* separates the fringe patterns due to the helium light of different wave lengths.

A more detailed view of the interferometer is shown in Fig. 3. The upper surface of the base plate *B* is a polished true plane. One side of the plate which projects about 0.3 mm above the upper surface of *B* forms a knife edge *SS* parallel to that surface, while the other side is undercut, leaving the edge *EF* parallel to *SS*, and the base *M* which forms a support for the sample *x*.

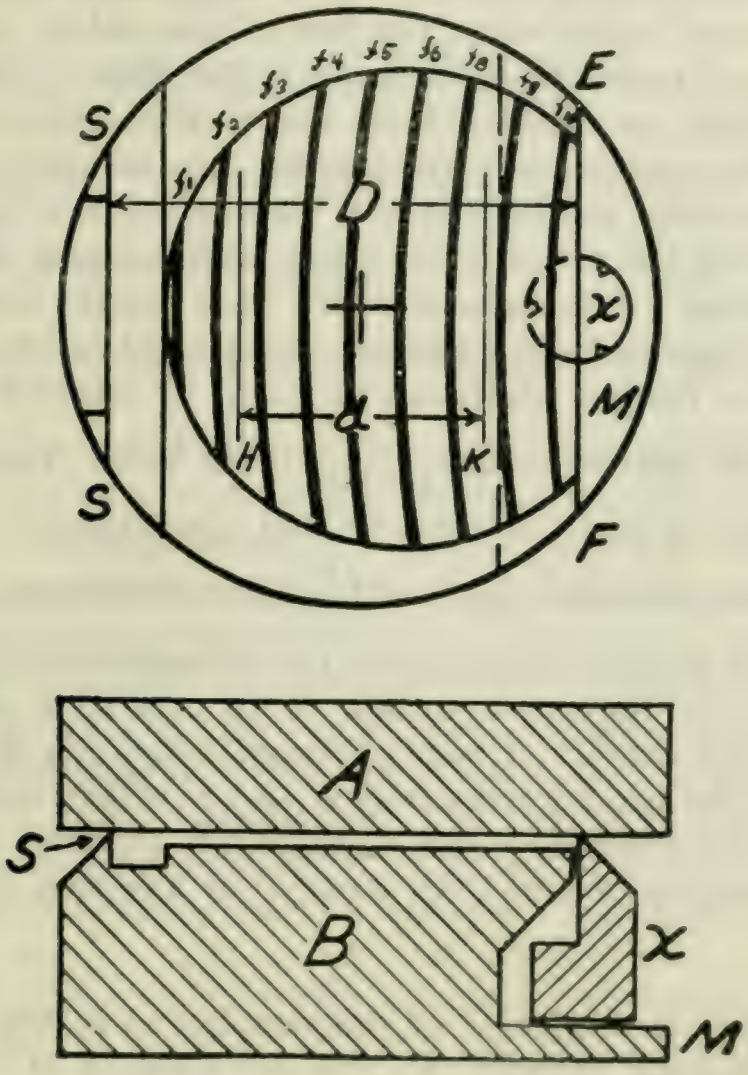



FIG. 3.—*Interferometer*

The upper end of the sample is cut away to the center from one side and bevelled to an edge from the other. The flat surface of the sample is placed in contact with the edge *EF*, thus assuring a constant distance *D* between the sample and the knife edge *SS*. Two reference lines *H* and *K*, distance *d* apart, are ruled parallel to the knife edge *SS* on the upper surface of the base plate.

The upper interferometer mirror *A*, which is a plate of glass with both faces polished true plane, rests on the knife edge *SS*

and the top of the sample $x$, adjusted to be slightly higher than $SS$. A narrow wedge-shaped space is thus formed between the two plates the widest part of which is toward $x$. Considering the two faces of this wedge, light from the lamp $H$ made parallel by the lens $O_1$, Fig. 2, falling upon the lower surface of $A$, Fig. 3, is in part reflected and the rest transmitted to the upper surface of $B$. Here again part of the light is reflected. Between these two reflected wave trains "interference" takes place. The observer, viewing this reflected light, sees straight dark bands parallel to each other across the face of the wedge. In Fig. 3, $f_1$, $f_2$, $f_3$, etc., represent these bands. The band $f_1$ shows that along that line the distance down and back between the plates is some whole number of wave lengths. On moving to a wider part of the wedge another line $f_2$ is reached where twice the distance between the plates is one wave length greater than at $f_1$. Similarly along $f_3$ this distance is two wave lengths greater than at $f_1$, etc. Starting from $f_1$ each successive band denotes that the separation of the two plates has increased by one-half the wave length of the light or about $\frac{1}{100\,000}$ of an inch. Therefore the total number of bands between $SS$ and $x$ multiplied by one-half the wave length of the light used $\left(\frac{\lambda}{2}\right)$ gives the difference in separation of the plates at $x$ and $SS$ or the difference in elevation of $x$ and $SS$ above the upper surface of $B$. As it is difficult to determine the number of bands between $x$ and $SS$, the number $N$ between the two reference lines $H$ and $K$ is determined. The corresponding distances $D$ and $d$ are known, therefore the difference in elevation of $x$ and $SS$ above $B$ at any time is equal to $\frac{\lambda D N}{2 d}$.

Let $L_x$ denote the length of the sample and $L_s$ the length of standard material between $SS$ and the plane of $M$. Let $\triangle L_x$ and $\triangle L_s$ represent the elongation of $L_x$ and $L_s$ caused by a rise of temperature $\triangle T$. If $L_x$ and $L_s$ expand differently the relative elevations of $x$ and $SS$ change, causing a change in the number of bands between $H$ and $K$. Let $N_1$ represent the number of bands between the reference marks before and $N_2$ the number after the temperature change takes place; then,

$$\triangle L_x = \triangle L_s + \frac{\lambda D}{2d}(N_2 - N_1) \qquad (1)$$

That is, the elongation of $x$ is equal to the elongation of $s$ plus the difference in elongation of the two, which is determined from the change in the number of bands between the reference marks.

The coefficient of linear thermal expansion is the elongation of unit length per degree rise of temperature

$$C = \frac{\triangle L}{L \triangle T} \qquad (2)$$

The coefficient of expansion of $x$ is then given by the expression

$$C_x = \frac{\triangle L_x}{L_x \triangle T} = \frac{\triangle L_s}{L_x \triangle T} + \frac{\lambda D (N_2 - N_1)}{2d L_x \triangle T} \qquad (3)$$

Since $L_x$ and $L_s$ are practically equal this becomes

$$C_x = C_s + \frac{\lambda D (N_2 - N_1)}{2d L_x \triangle T} \qquad (4)$$

Where $C_s$ is the coefficient of expansion of the base plate material.

In order to control the temperature properly the interferometer was mounted on a steel block $G$ in the bottom of the container $C$, Fig. 4, which consisted of a steel tube, 30 cm long, 5 cm in diameter, and 1 mm thickness of wall, the upper end of which was closed with a glass window $W_1$; 10 cm from the base another glass window $W_2$ was supported by a heavy brass ring. Most of the lower part of the tube was cut away to allow easy adjustment of the interferometer. This end of the tube was closed with a steel cup $R$ which screwed onto the tube at $U$ with a rubber gasket to make the joint tight. A little mercury in the bottom of the cup made good metallic contact between the base block and the bath. The container was lowered with a rack and pinion into the oil bath which regulated the temperature. The bath liquid was circulated through the tubes $D$ and $E$ by the propeller $P$. To eliminate vibration the motor $M$ was supported on a separate base and connected to the propeller shaft by a small rubber tube. The liquid was cooled by the brine coil $K$ and heated with a 10-ohm resistance coil $H$ the current in which was regulated by a relay operated by the thermostat $J$. This apparatus was thermally insulated with ground cork and mounted in a wooden box.

The temperature of the liquid around $C$ could be held for any length of time within 0.01° of the desired value. The tempera-

ture of the bath was read with a thermometer $T$ and a five-junction thermocouple $L$, and the temperature of the base block and sample with another five-junction thermocouple $N$. A temperature survey was made of this apparatus with differential

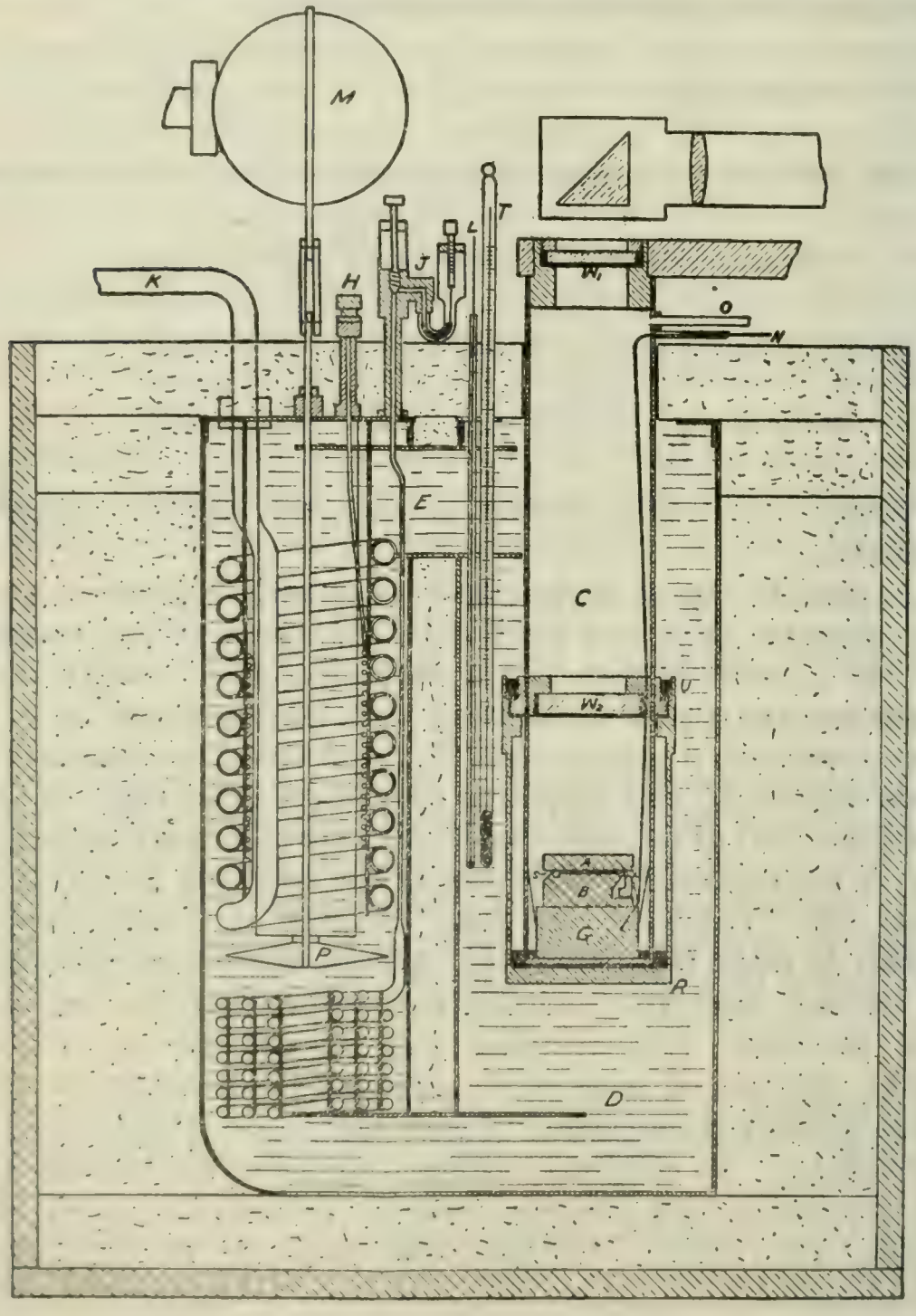



FIG. 4.—*Temperature control apparatus*

thermocouples to determine both the time required for the interferometer and sample to reach a steady state when the temperature of the bath was held constant, and the lag of the sample when the bath temperature was changing.

## 2. EXPERIMENTAL PROCEDURE

The amalgam material after being prepared in the manner already described was made into samples about 6 mm in diameter and 1 cm long, illustrated by *x*, Fig. 3. These samples were kept for several weeks before measurements were made. The porcelain samples were made in the same form and kept under water. The tooth specimens were taken from different teeth and different parts of the same tooth. One of the samples, the expansion of which is shown in Fig. 5, was taken from the crown of a large molar, the other from the root of a long cuspid.

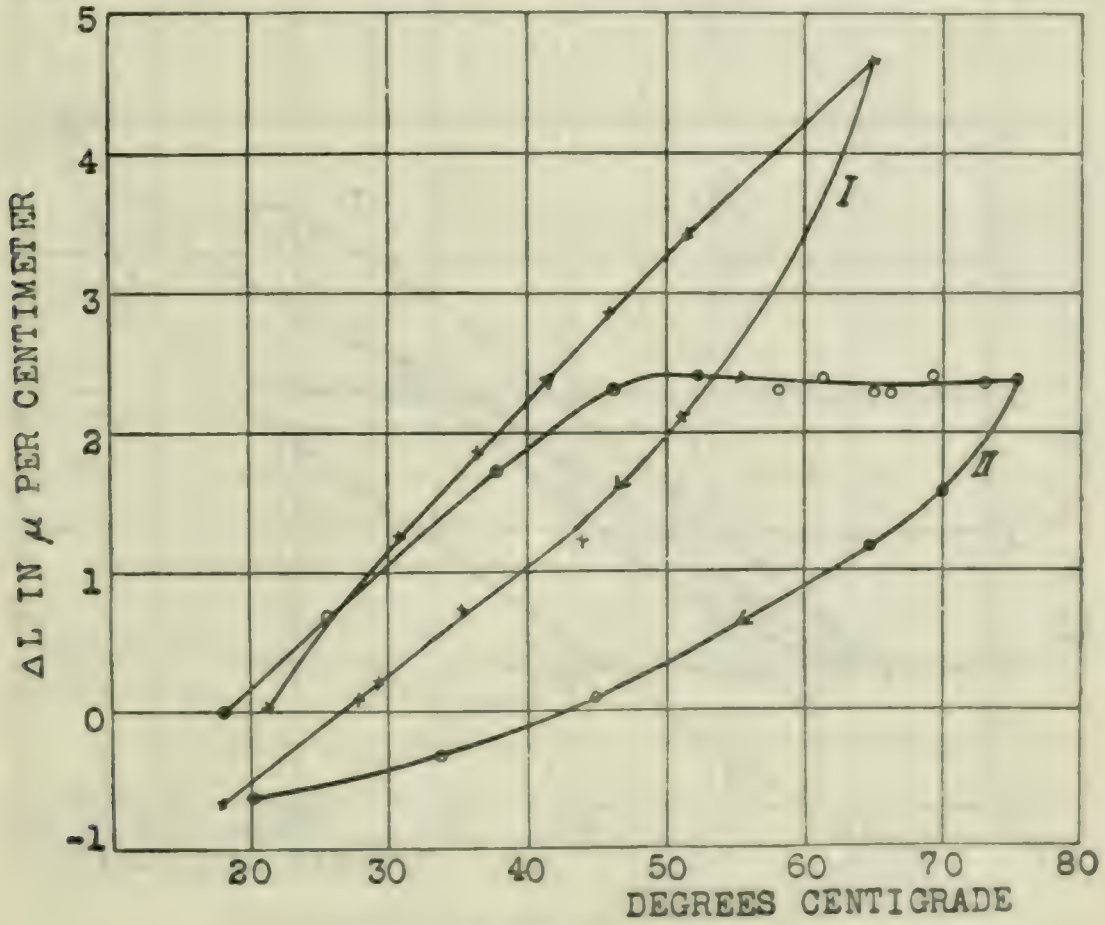



FIG. 5.—*Thermal expansion of teeth*

(I—crown. II—root)

After the sample was properly adjusted the interferometer was placed in the container and lowered into the bath. Two procedures were followed in making the measurements. The first was to hold the temperature of sample constant for at least one hour at each point before the measurements were made. The second was to change the temperature of the sample slowly, about 1° C in three or four minutes, and make observations periodically.

With the samples from teeth it was found that as soon as they were heated moisture evaporated and a very rapid contraction

took place amounting to 0.2 to 0.3 mm for a 1-cm sample. These samples regained their original length if allowed to stand in water for two or three days. To overcome this contraction, which was many times greater than the thermal expansion of the material, the interferometer and sample were placed in a container filled with water. This container was then placed in the temperature-control apparatus. With both the porcelain and teeth it was found necessary to keep the samples under water and make the measurement with the samples under water in order to obtain

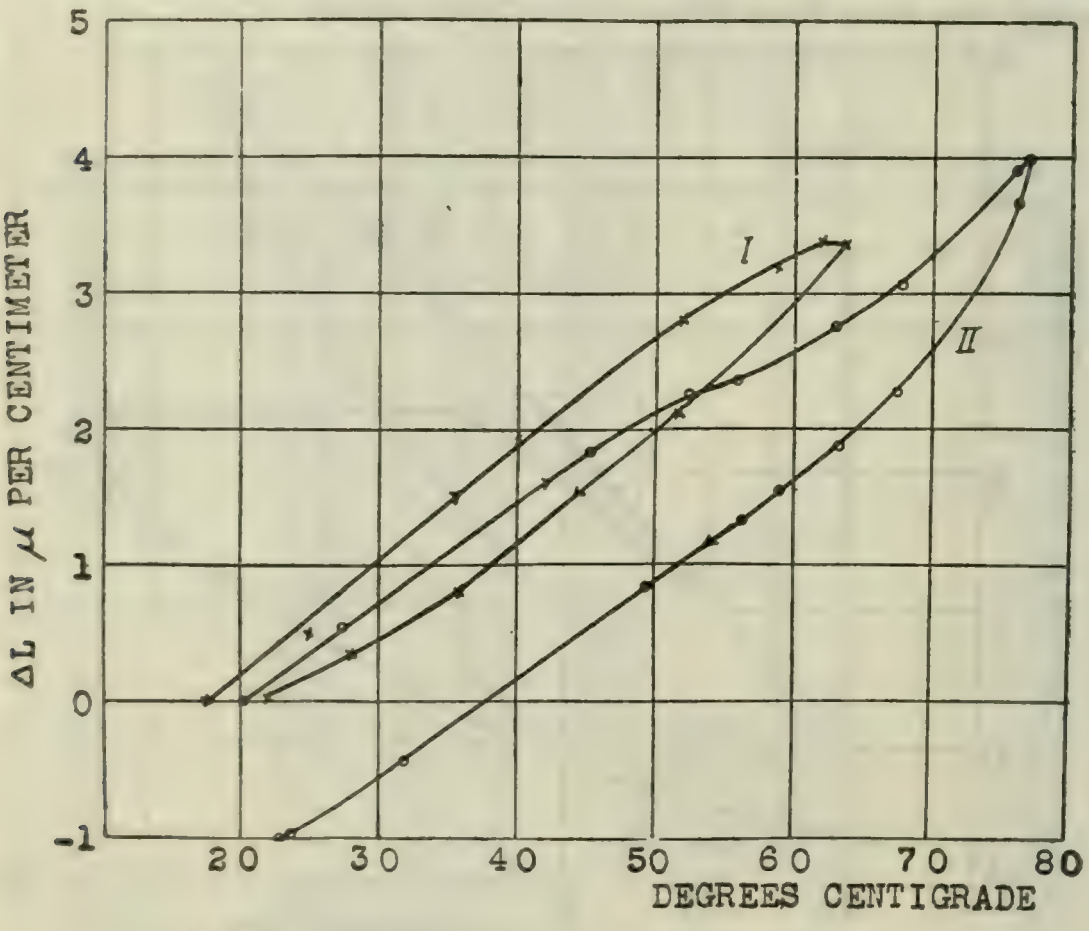



FIG. 6.—*Thermal expansion of synthetic porcelain*

consistent results. This procedure seems to reproduce actual condition of the mouth and yield values of thermal expansion as near correct as it is possible to obtain with this type of material.

### 3. RESULTS

The following curves represent the elongation of the different materials with change of temperature. Degrees centigrade are plotted as abscissae and change in length ($\Delta L$) in microns ($\mu$) of a sample 1 cm long as ordinates. All the observations that were taken have been plotted, none were rejected or omitted.

Curve *I*, Fig. 5, is for a sample cut from the crown of a molar, Curve *II* for a sample from the root of a newly extracted cuspid.

Curves *I* and *II*, Fig. 6, represent the expansions of two different samples of porcelain.

The curves in Figs. 7 and 8 are for different kinds of amalgams. These curves are lettered to correspond with kind of material from which the samples were made. In fact, most of the samples had previously been used for experiments of setting changes.

Most of the samples showed irregular behavior near 80° C. Some of the samples when removed from the container were

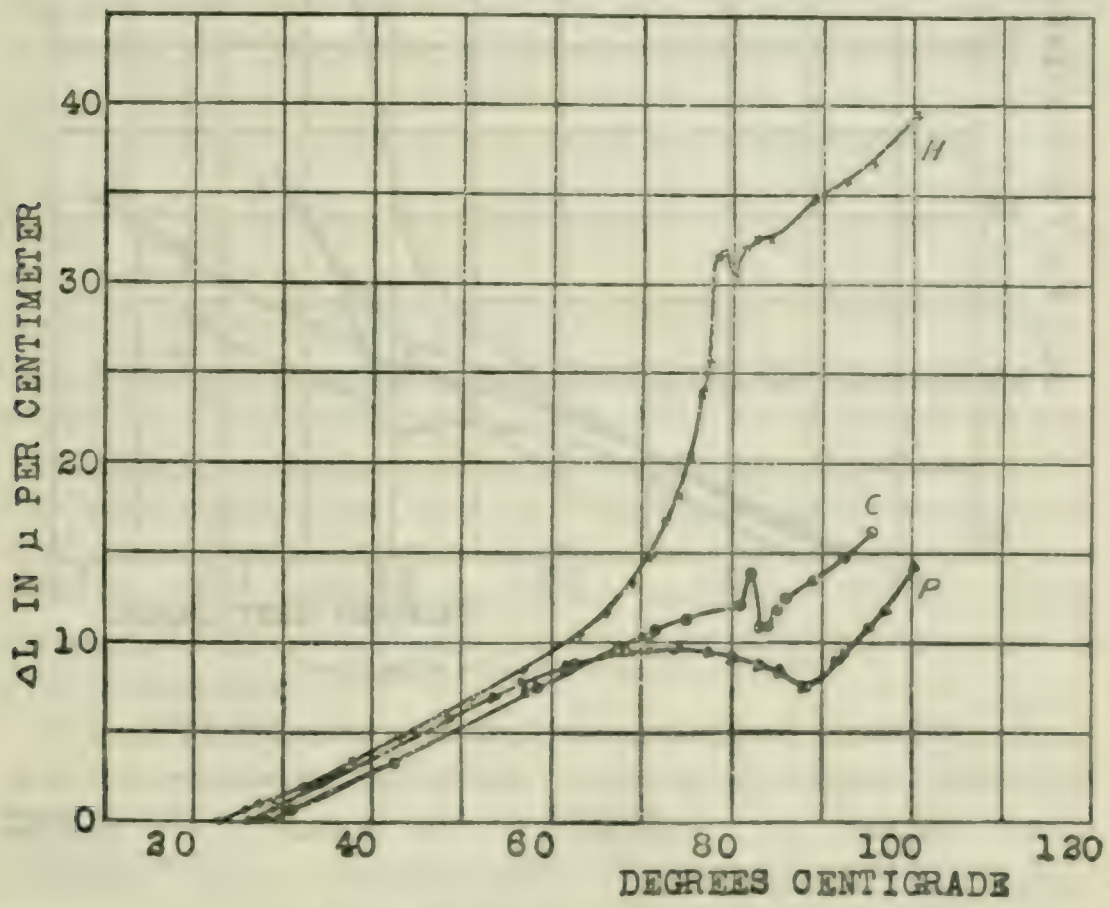



FIG. 7.—*Thermal expansion of amalgam*

covered with soft drops of mercury which formed into bright crystals in a short time. An inspection of these curves and the samples showed that the amalgams must have undergone some radical transformations when heated. It is very probable that any filling or part of a filling, if by chance subjected to temperatures near this value, may suffer serious injury or have its physical properties entirely changed.

In Table 1 there are tabulated data on the linear thermal expansion of a number of materials, including sections of teeth.

From this table it is seen that the expansions of teeth range from 6.4 to 11.4, depending upon the tooth selected and the portion of the tooth used, an average value of approximately 8. The porcelain average value is not far from the above figure, gold is somewhat higher (14.4), while the amalgams average about 25.

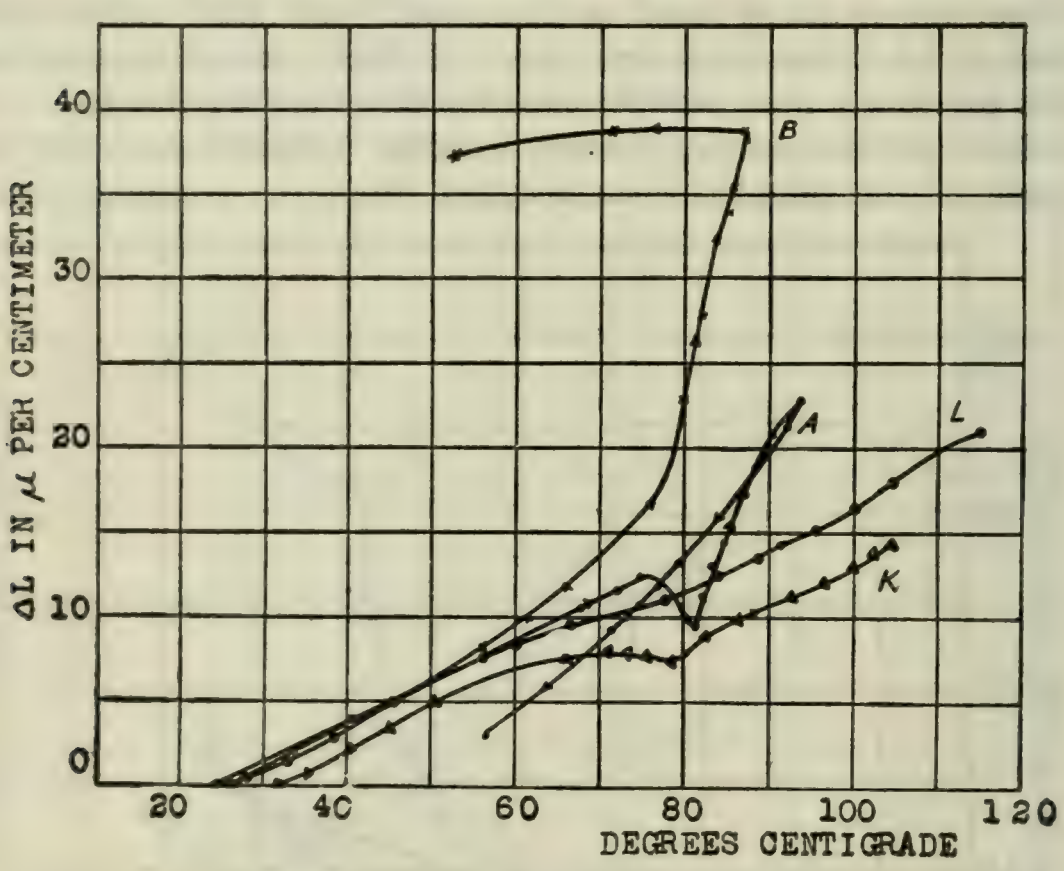



FIG. 8.—*Thermal expansion of amalgams*

**TABLE 1.—Average Expansion Coefficients, Range 20 to 50° C**

| Material | Expansion coefficients x $10^6$ | Material | Expansion coefficients x $10^6$ |
|---|---|---|---|
| Tooth (root) | 8.3 | Amalgam (C) | 25.0 |
| Tooth (across crown) | 11.4 | do | 24.7 |
| Tooth (root and crown) | 6.4 | do | 28.0 |
| Do | 8.7 | Porcelain (Bayeux) | 4.1 |
| Do | 8.3 | Gold | 14.4 |
| Synthetic porcelain | 7.1 | Platinum | 9.0 |
| Do | 8.1 | Silver | 19.2 |
| Do | 7.5 | Mercury (linear) | 60.6 |
| Amalgam (H) | 26.4 | Zinc | 29.2 |
| Amalgam (C) | 25.0 | Tin | 22.3 |
| Amalgam (K) | 22.1 | Copper | 16.8 |
| Amalgam (P) | 24.5 | Gutta-percha | 198.3 |
| Amalgam (A) | 25.4 | Aluminum | 23.1 |
| Amalgam (B) | 28.0 | Steel | 11.0 |
| Amalgam (L) | 24.8 | | |

Since the effects due to the differential expansions of the materials depend upon the temperature range, size of cavity, and elasticity of tooth substance and material, no general statement should be made regarding the relative merits of materials unless all the important conditions are given due consideration.

To illustrate, let us consider the case of a maximum cavity and filling 1 cm in diameter, undergoing a temperature variation of 50° C. Then the free expansion along each coordinate axis is 4 microns for the cavity, 7 microns for the gold filling, and 12.5 microns for the amalgam. (If the dimension or temperature range is less, these effects will be proportionally reduced.) If we have perfect adaptation and no stress at the lower temperature, then at the higher temperature there are two extreme possibilities: (*a*) The elasticity of the tooth and compressibility of the material may be such that perfect adaptation is maintained, or (*b*) the rigidity of the tooth and plasticity of the material may be such that there will be a flow of material in the only free direction causing a spheroiding or bulging over the cavity. With a perfectly rigid tooth cavity this may equal three times the linear differential expansion of the substances, which will be 25 microns in the case of amalgam. Should the filling material take a permanent set at the higher temperature, then on returning to the lower temperature, all materials having undergone free contraction, there is a possibility of a 4-micron separation around the filling. This is analagous to the case of heating the Wedelstaedt tube referred to in a previous section.

The above temperature range of 50° C has been decided upon as a fair representation of the temperature variation to which metallic fillings may be subjected. In order to test this experimentally, copper-constantan thermocouples were cemented into amalgam inserts 1 to 3 mm from the surface, and the temperatures of the inserts were read by means of a potentiometer when different foods and drinks were taken into the mouth. With ice water and cracked ice temperatures as low as 5° C and with hot foods and drinks temperatures from 50 to 60° C were observed in the inserts. No unusual or excessive sensation of pain was indicated by the adjacent vital teeth during the experiments.

## V. DIMENSIONAL CHANGES WITH TIME

### 1. APPARATUS

The apparatus described in the previous section was used to measure the dimensional changes of newly made amalgam samples during the hardening or setting period. The temperature of the sample and interferometer was held constant and the variations in the length of the specimens with time were recorded. These dimensional variations during hardening will be referred to as setting changes.

In equation (1), $\Delta L_s$ represents the change in the length of the material under the knife-edge, due to the change in temperature. In the present case the temperature was constant, therefore $\Delta L_s$ equals zero and the expression for the setting change of the sample becomes

$$\Delta L_x = \frac{\lambda}{2}\frac{D}{d}(N_2 - N_1) \qquad (5)$$

Here the interferometer becomes a lever of the second class with the knife-edge forming the fulcrum, the top of the sample the point of application of the force, and the upper plate, which weighs about 10 grams, the load. This type of lever is far less susceptible to friction and contact error than those used in the moving dial or mirror instruments. The only restraining force on the sample is the constant 5 grams weight of the cover plate.

The results obtained from several samples made from the same material and held constant at temperatures ranging from 8 to 37° C showed that careful temperature control was not of sufficient importance to warrant the use of the constant temperature apparatus.

Four interferometers of different construction were mounted in a semicircle on a table so that the Pulfrich apparatus could be turned from one to another for making observations on the interference fringes. A thermometer was placed close to the interferometers and the temperature of the room was recorded after each observation on the fringes. This arrangement greatly facilitated the work, for four samples were investigated simultaneously, whereas the constant temperature apparatus accommodated only one at a time.

## 2. EXPERIMENTAL PROCEDURE

The alloys were amalgamated and condensed into the mold according to the procedure previously described. The specimens were immediately removed from the mold and adjusted to fit the interferometer, which required from 4 to 8 minutes. The cover plate was pressed down upon the sample with a force of several pounds to insure good contact at the bearing points and to ascertain whether or not the sample had hardened enough to support the weight of the plate. Most of the samples hardened in a few minutes, but a few like *M* and *N*, Fig. 14, were still quite soft after 60 minutes. The time record started the moment the sample was removed from the mold and observations of the length changes, which commenced immediately after the adjustment of the samples, were taken at given intervals over a period of one to several days. With rapidly changing materials of this kind the number of interference bands between the reference lines was estimated to the nearest 0.1 of a band. Since 0.2 of a band is equivalent to about 0.05$\mu$ this estimation gave all the accuracy necessary.

At least three samples from each material were investigated according to the above procedure.

## 3. RESULTS

The following curves represent length changes which took place during setting. Time in minutes is plotted as abscissae and change of length ($\Delta L$) in microns ($\mu$) of a sample 1 cm long as ordinates. An ascending curve represents an elongation and a descending curve a contraction. The time required to adjust the sample to the interferometer is plotted along the zero ordinate. The mean temperature and maximum variation in temperature of each sample have been recorded with the curve.

In Fig. 9 are represented the setting changes of four samples from material *C*. The samples were all prepared according to our regular procedure but were held at different temperatures after being placed in the interferometer. The temperatures at which the different samples were held during the runs are as follows: Sample *C–1* at 37° C, *C–2* at 27.8° C, *C–3* at 20.4° C, and *C–4* at 8° C.

Fig. 10 represents the data taken on four samples of material *B*. The samples were prepared according to our regular manipulation and held very near to the same temperature throughout the ex-

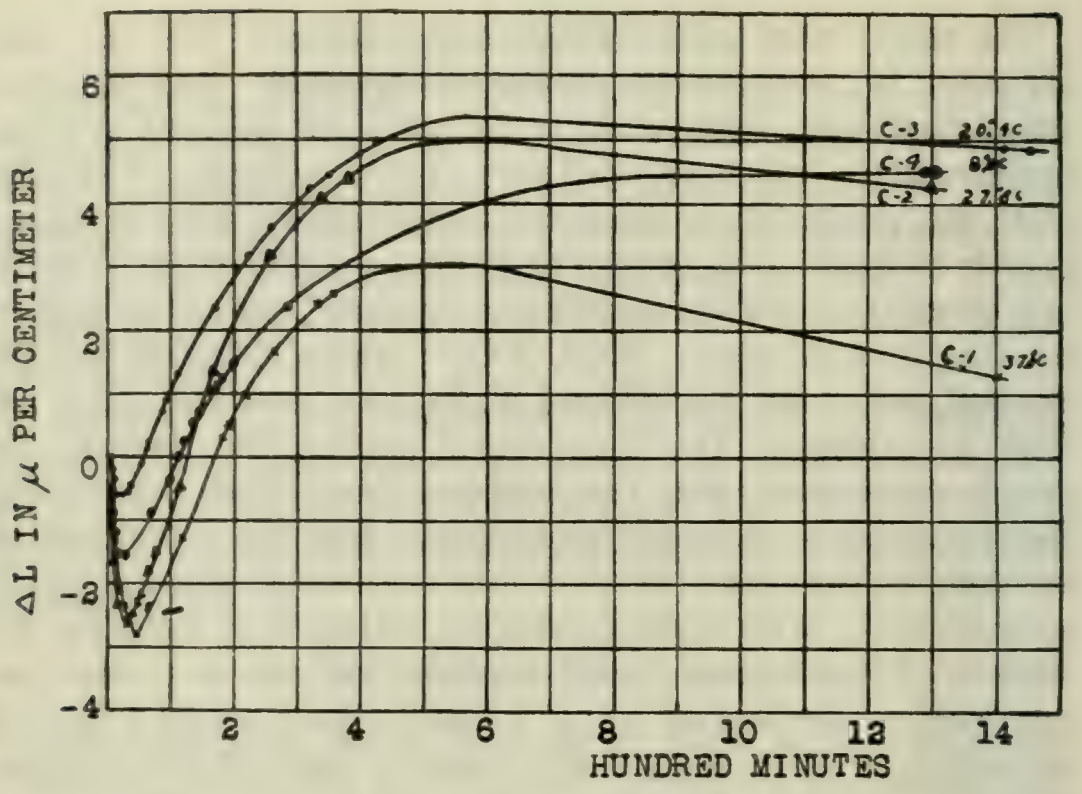



FIG. 9.—*Setting changes of amalgam C*

Specimens held at different temperatures

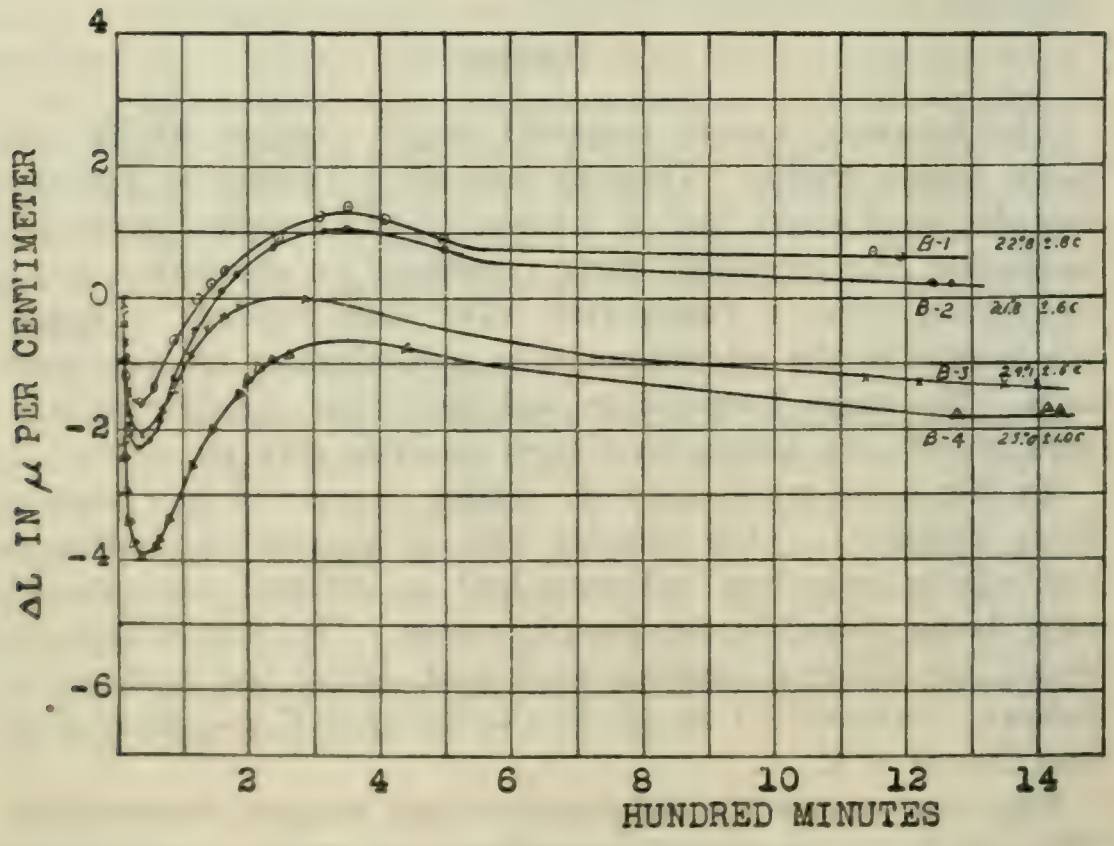



FIG. 10.—*Setting changes of amalgam B*

Specimens held at nearly the same temperature

periments. The mean temperature of the sample and the maximum variation during the run are recorded with each curve. Figs. 11 to 13 represent the results obtained from samples of alloys *C*, *H*, and *A*, which had been given various treatments before and subjected to similar conditions after condensation. The mulling time was varied from 1 to 35 minutes. A specimen of each alloy was cooked for three hours at 120° C, and 1⅔ per cent zinc was added to one alloy.

From the foregoing curves it is seen that the length of time devoted to mulling the amalgam exerted by far the greatest effect upon its subsequent behavior. The curves from samples of mate-

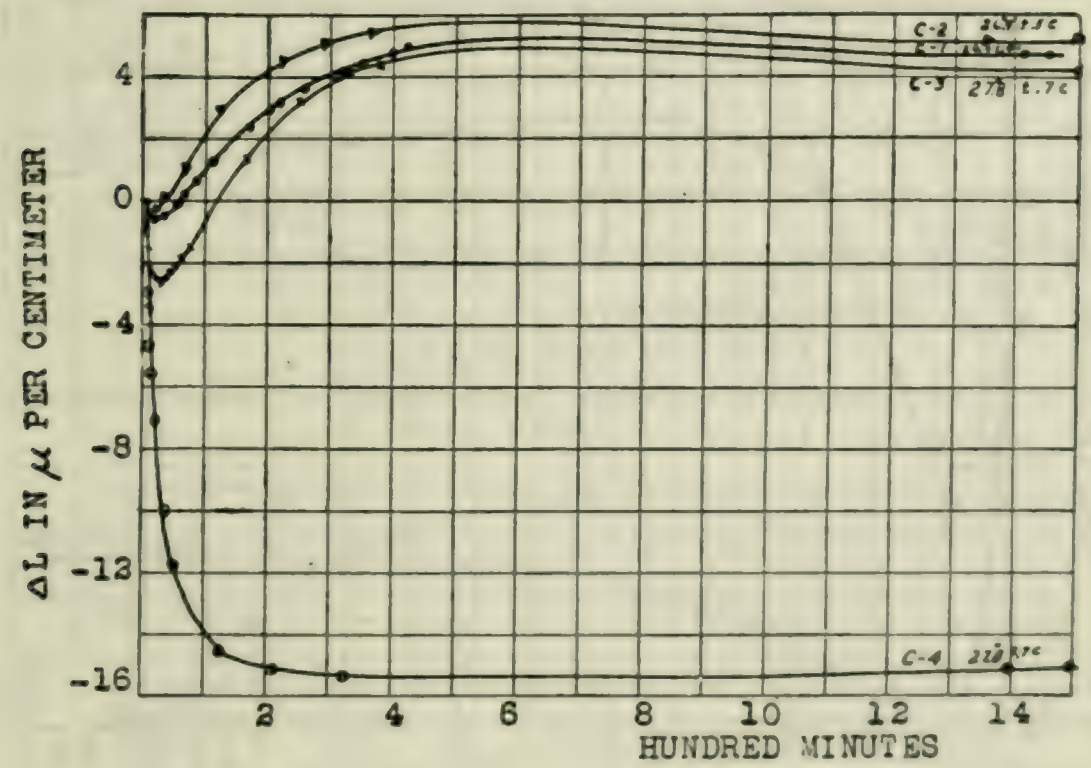



FIG. 11.—*Setting changes of amalgam C*

C-1, Usual manipulation; C-2, alloy cooked 3 hours at 120° C; C-3, mulled 1 minute; C-4, mulled 35 minutes

rial *B*, Fig. 10, which received practically the same treatment, while quite concordant, do not show a much better agreement than those of material *C*, Fig. 9, which were held at different temperatures during the setting period. In Figs. 11, 12, and 13 curve 1 represents the usual manipulation. Curve 2, in which alloys were cooked for three hours at 120° C, differs very little from curve 1. *C*–3 and *H*–3, which were mulled only one minute, agree almost as well with curve 1. The addition of 1⅔ per cent zinc to alloy *A* seems to have changed the character of the setting curve *A*–3. The marked effect caused by mulling the amalgams 20 to 35

minutes is shown by curve 4. Experiments of this kind showed that large setting contractions could be produced in any of the amalgams by overmulling and emphasized the importance of that part of the process. Compared with this effect the slight irregularities due to variations in room temperature seem to be insignificant. If setting contractions of 10 to 20$\mu$ per centimeter are important, then this question of mulling time must be given careful consideration.

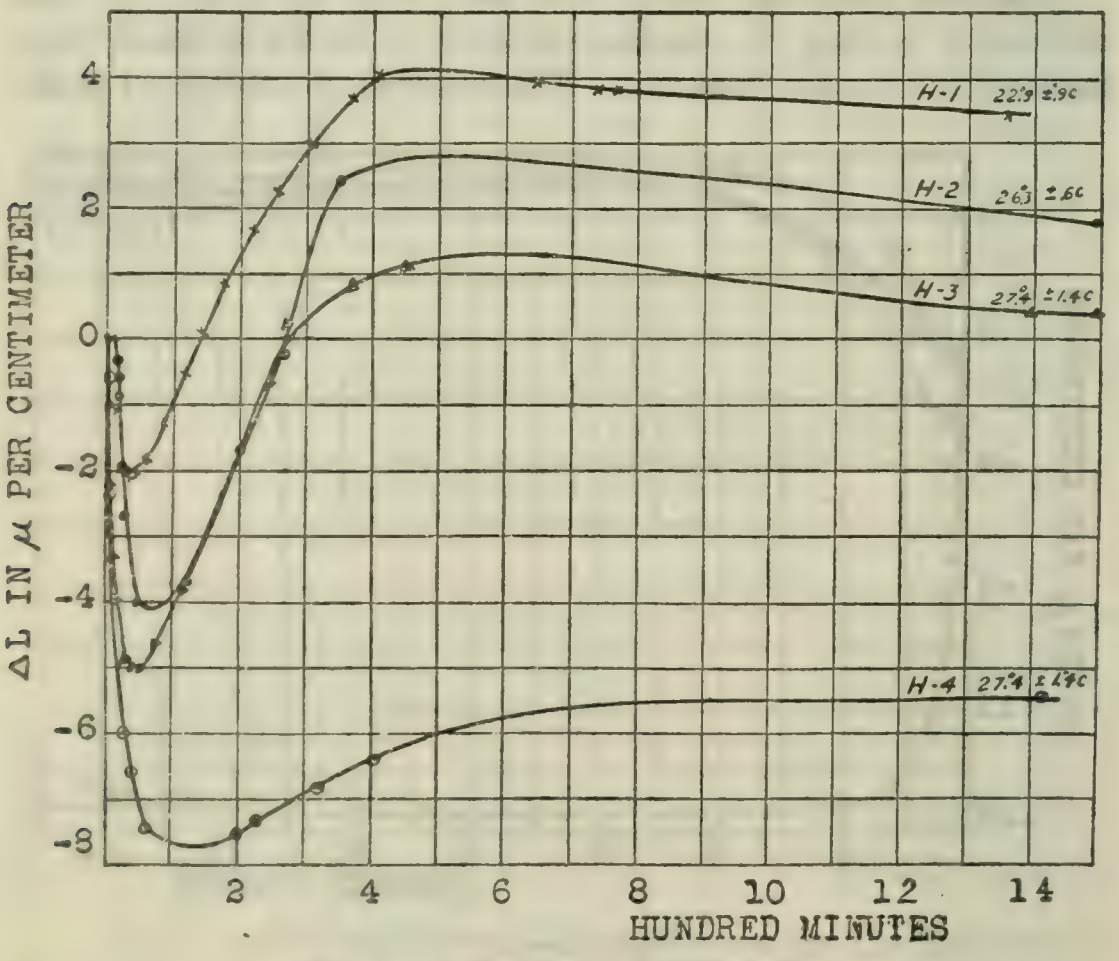



FIG. 12.—*Setting changes of amalgam H*

H–1, Usual manipulation; H–2, alloy cooked 3 hours at 120° C; H–3, mulled 1 minute; H–4, mulled 25 minutes

Our results upon effects of mulling agree very well with the findings of Dr. Gray.[5] He has placed greater emphasis upon the importance of accurate temperature control of the samples during the setting period than we have. Regarding the effect of annealing no comparison can be made because he has neglected to state the temperature at which the annealing was carried out.

The setting changes of each of the other materials are shown in Figs. 14 to 17. At least three samples from each material pre-

[5] Gray, Journal of the National Dental Association, 6, 10, p. 917; 1919.

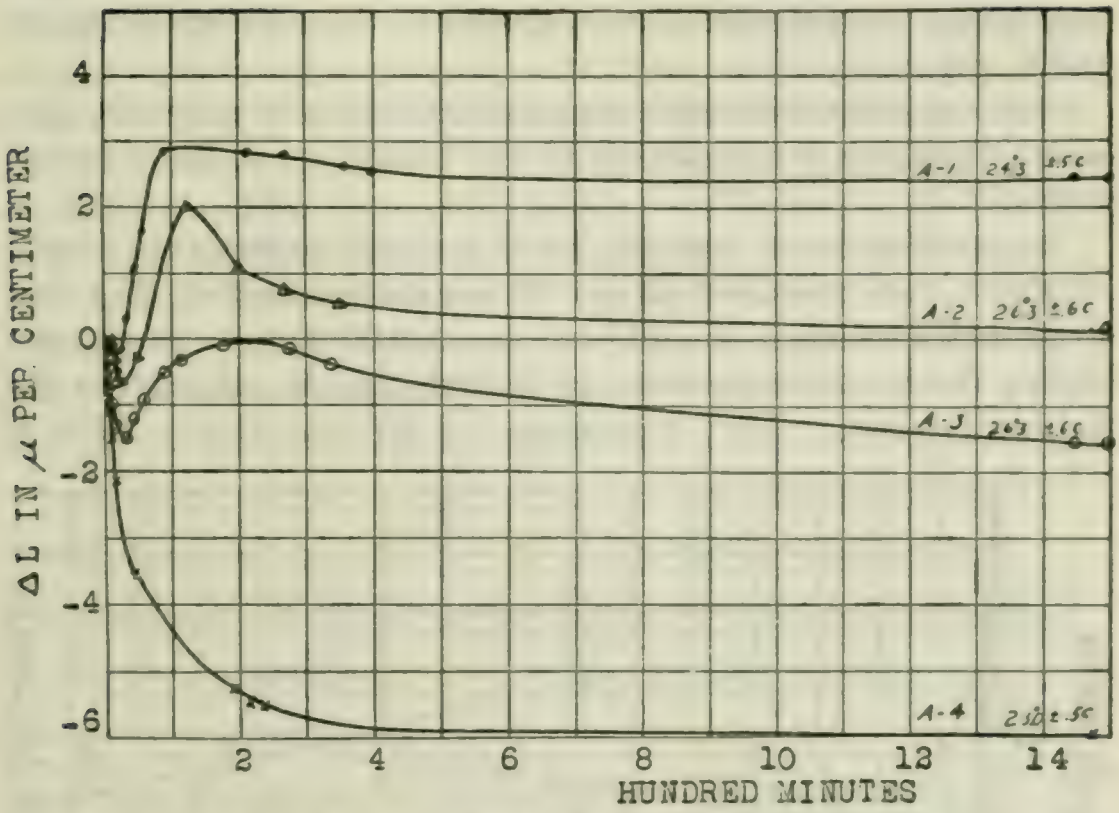



FIG. 13.—*Setting changes of amalgam A*

A-1, Usual manipulation; A-2, alloy cooked 3 hours at 120° C; A-3, 1% Zn added to alloy; A-4, mulled 20 minutes

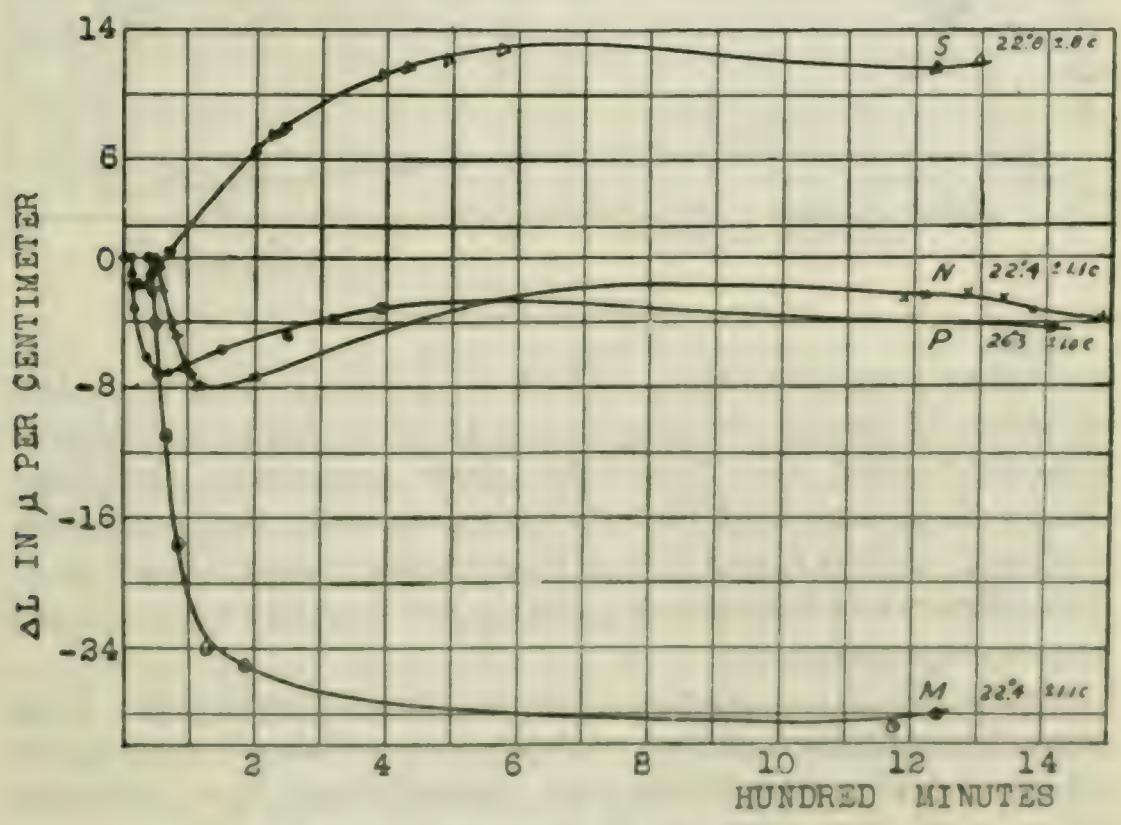



FIG. 14.—*Setting changes of amalgams*

pared according to the regular procedure were tested and gave concordant characteristic curves similar to those shown for material *C*, Fig. 9.

Only one curve from each material has been plotted for the purpose of making a comparison of the behaviors of the different material.

From the chemical analysis, Table 3, it will be seen that *M* and *N*, Fig. 14, are low silver alloys. These specimens were very slow in setting; in fact, it was impossible to make any measurements during the first hour because the material would not support the lightest pressure. Alloy *S* contained 73 per cent silver. Alloy *P*

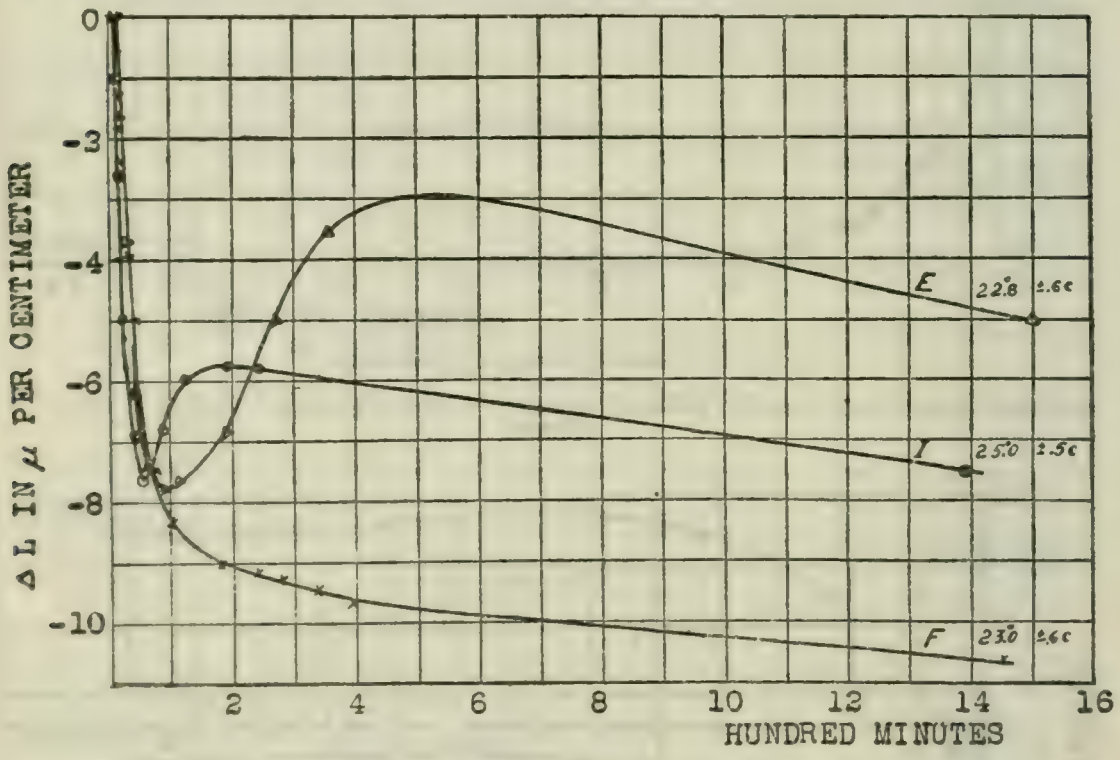



FIG. 15.—*Setting changes of amalgams*

contained 5 per cent zinc. Alloys *E*, *I*, and *F* are not widely different in setting changes during the first hour, but diverge somewhat after this time. All show permanent shrinkage. Alloys *B*, *G*, and *T* of Fig. 16 have practically the same silver analyses. Alloys *K* and *L*, Fig. 17, are lower in silver than *E* or *F*. The difference in behavior is probably due to relative percentages of two other elements.

Nearly all of the samples show an initial contraction. With some this continued and no recovery was evidenced; with others an initial contraction of from 1 to 3 microns took place in the first 30 or 40 minutes, after which the sample expanded for the next 400 minutes, remaining quite constant during the remainder of

the experiment. The initial contraction could be due to one or all of at least three causes. The sample is usually quite soft for a few minutes, which might cause a settling of the sample under even its own weight; there might be a real contraction of the material; or in adjusting the sample it is heated somewhat in the hand, which is slightly above the room temperature. In the last case a thermal contraction should take place during the first few minutes.

To follow the actual temperatures of the sample during the setting or hardening period, one junction of a differential thermocouple was placed in a block which had the same temperature as the

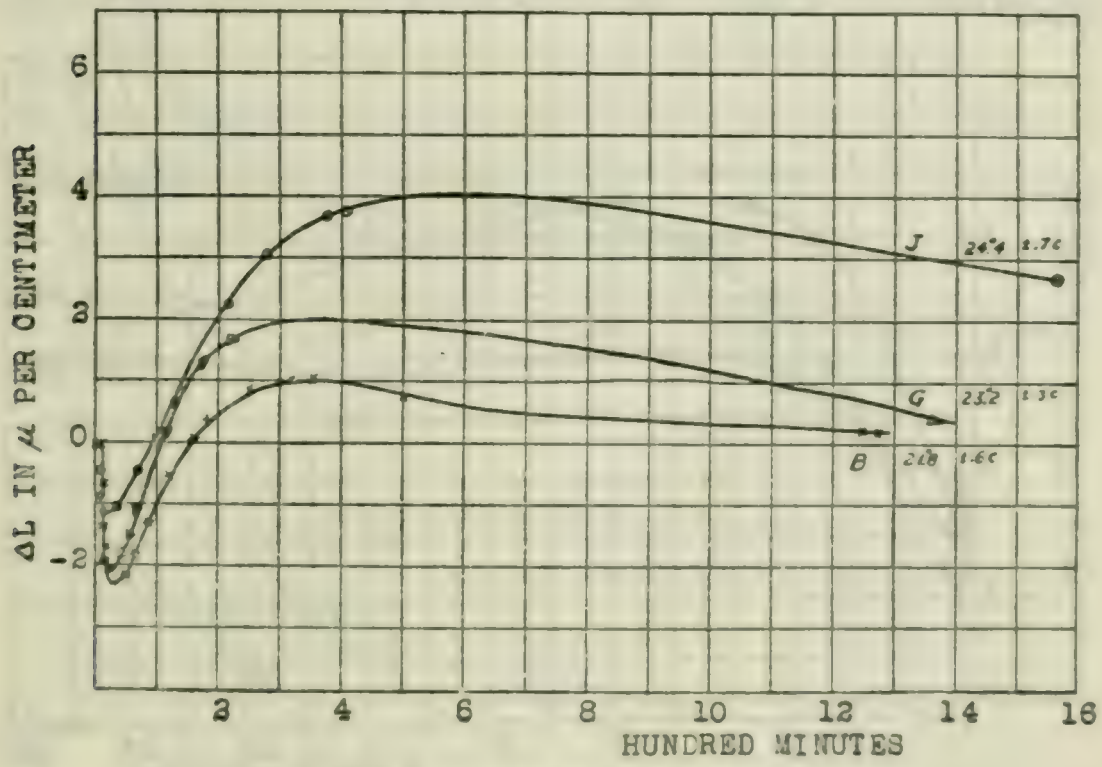



FIG. 16.—*Setting changes of amalgams*

room. The other junction was packed in the center of the sample which was made and adjusted according to the usual procedure.

Measurements made immediately after samples were placed in the interferometer showed that their temperatures were 4 to 8° C above the temperature of the block which was very nearly 22.5° C during these experiments. Fig. 18 shows the cooling curves of some of these samples. The sample *19–A* was 3.5° C above the temperature of the block when placed in the apparatus and was still 0.7° C above the temperature of the block 150 minutes later. Three hours later it was warmed 8° C above block temperature and allowed to cool. Curve *19–B* shows that it returned to the block temperature after 22 minutes.

The second sample was 7.4° C above block temperature immediately after being put into the apparatus. Its cooling is shown by curve *16–A*. It was still 0.5° C above block temperature 60 minutes later. The following day its temperature was increased 5° C. It then cooled in 12 minutes as shown by curve *16–B*.

Curve *4* shows another sample that required 80 minutes to return from 5° C above to block temperature.

These experiments show that heat is evolved by the material during the amalgamation. This evolution of heat seems to continue during the period while the sample is undergoing most of its variation of length. Of course some of the original heating

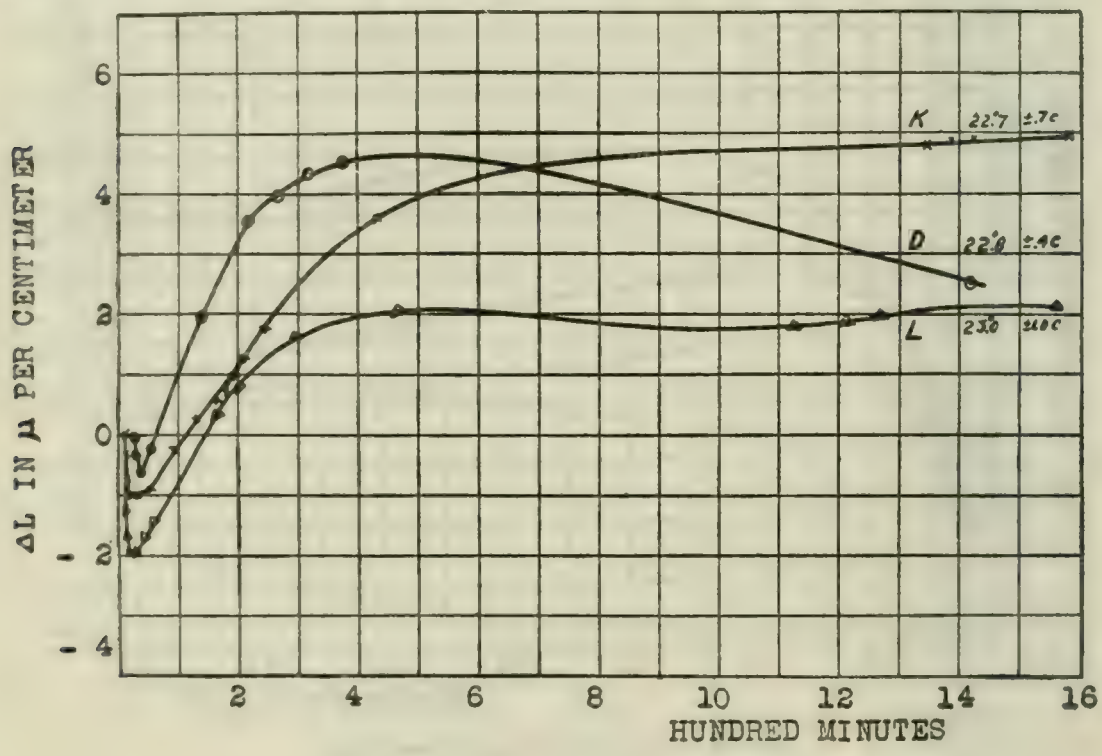



FIG. 17.—*Setting changes of amalgams*

comes from the hand of the operator, but curves *19–B* and *16–B* show that the sample should return to the temperature of the room in 15 to 20 minutes. Enough heat seems to be evolved to keep the temperature of the sample above that of the surroundings for several hours. From this it seems that careful control of the sample container does not insure that temperature of the sample is the same as that of its surroundings. Consideration of the foregoing results make it possible to account for 1 to 2 microns of this initial setting contraction by the thermal contraction of the material. The fact that some of the samples, which hardened in a few minutes after condensing, contracted more than that

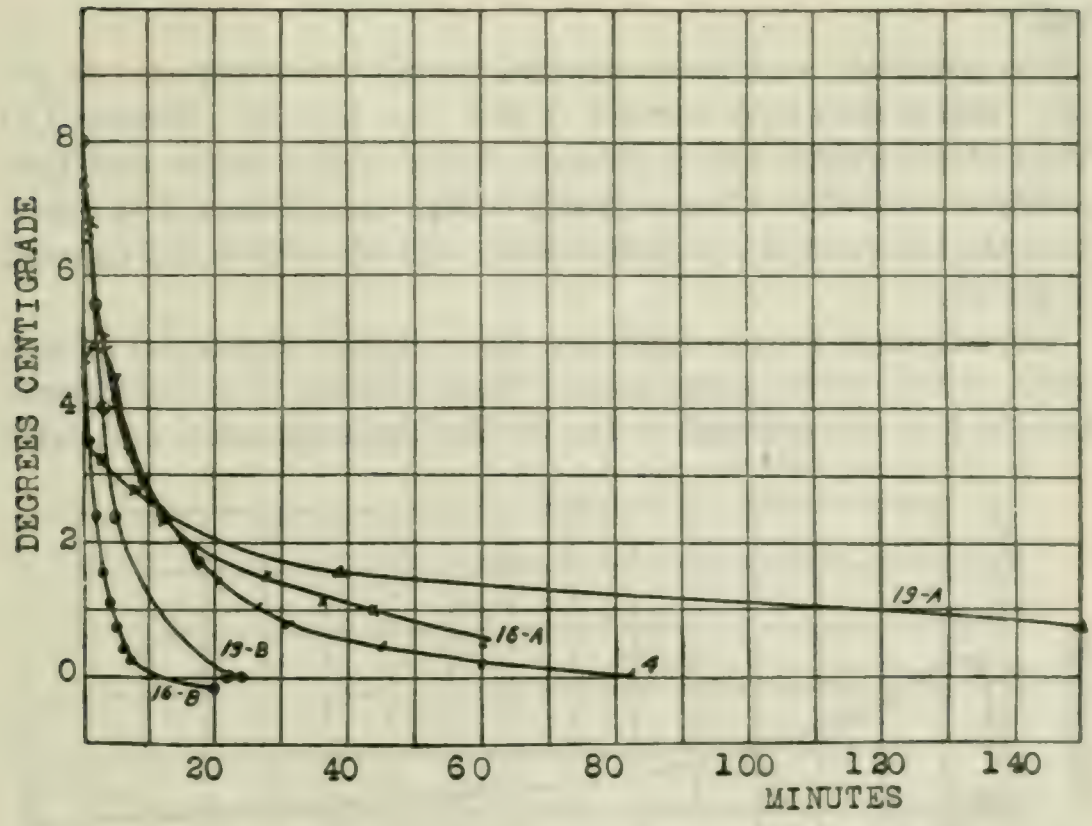



FIG. 18.—*Cooling of amalgams during and after setting*

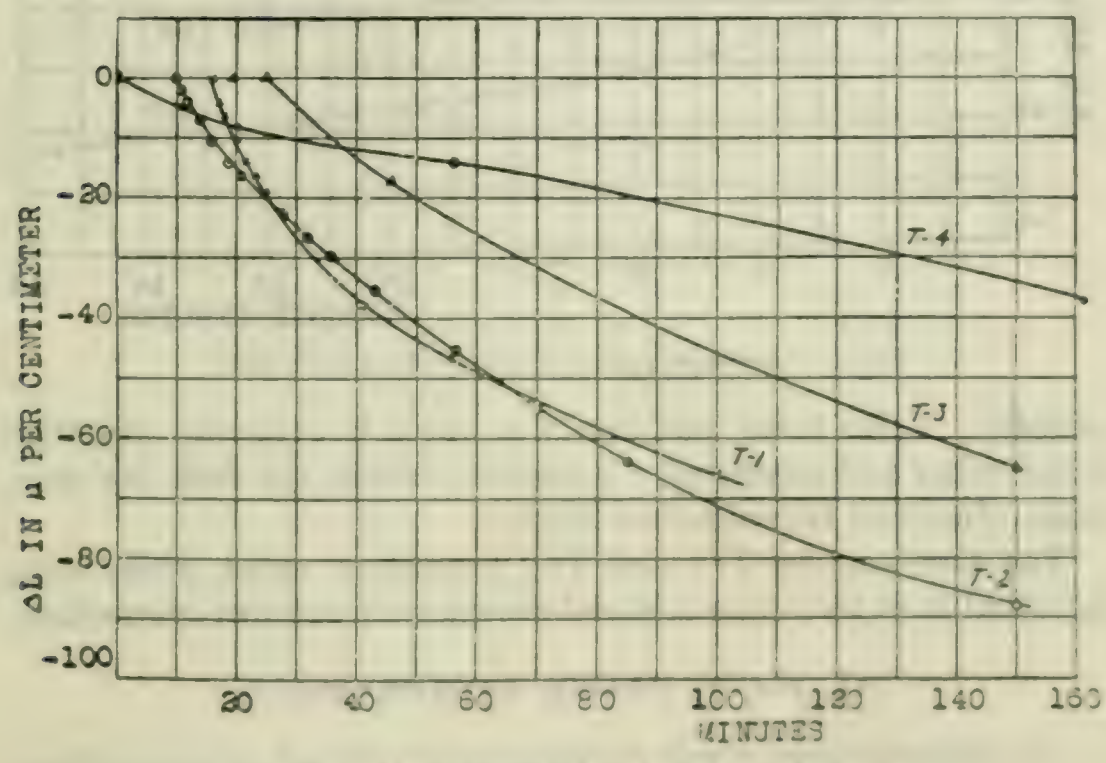



FIG. 19.—*Setting changes of synthetic porcelain in air*

amount leads us to believe that part of the initial contraction was real.

The porcelain samples contracted rapidly when exposed to the air. This is shown by curve *T–1* and *T–2*, Fig. 19. Sample *T–3* retained its length for 25 minutes while under water and then contracted rapidly when exposed to the air. Curve *T–4* represents the behavior of a sample coated with its varnish and exposed to the air.

The curves in Fig. 20 represent the behavior of samples of porcelain which were kept under water during the experiment. Sample *T–5* was exposed to the air during adjustment and dried

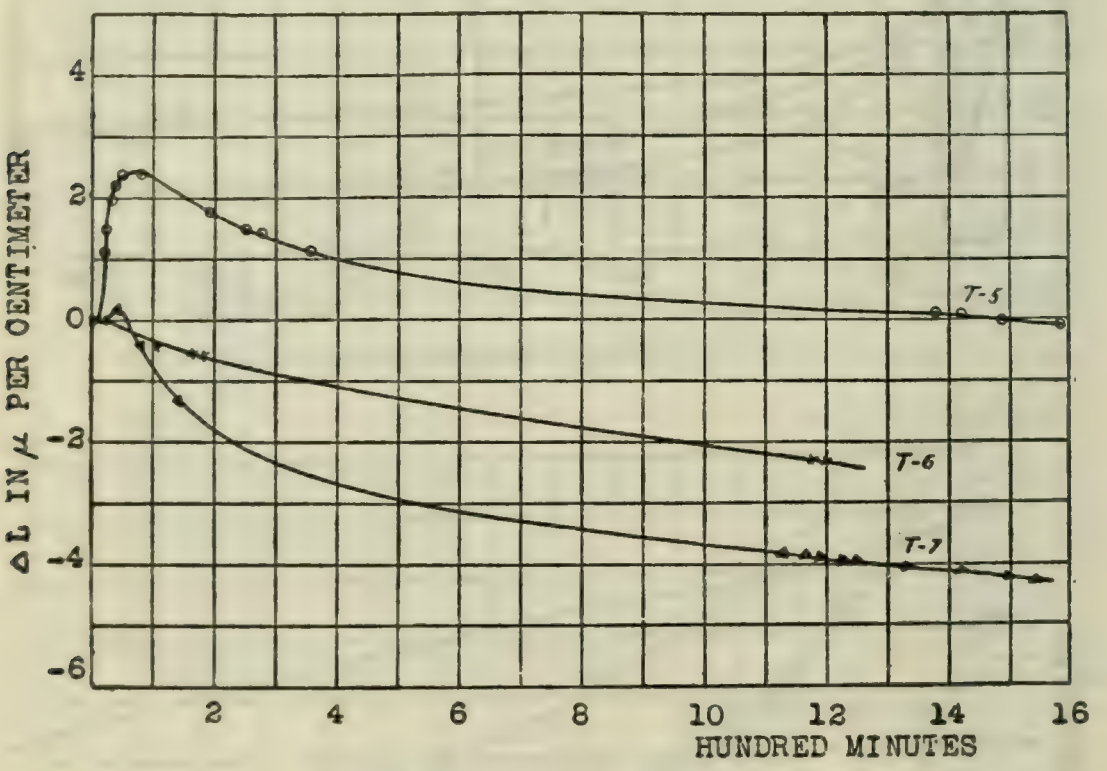



FIG. 20.—*Setting changes of synthetic porcelain in water*

slightly. Upon being put into the water it evidently absorbed some water and expanded 2.4 microns during the first few minutes; after that it contracted slowly.

The two samples *T–6* and *T–7* were kept moist while being adjusted to fit the apparatus and show a slow uniform contraction.

## VI. FLOW UNDER COMPRESSION

The authors have found all amalgams yielding under constant pressure even months after amalgamation. Hence the questions of setting and crushing strength become relative factors. When

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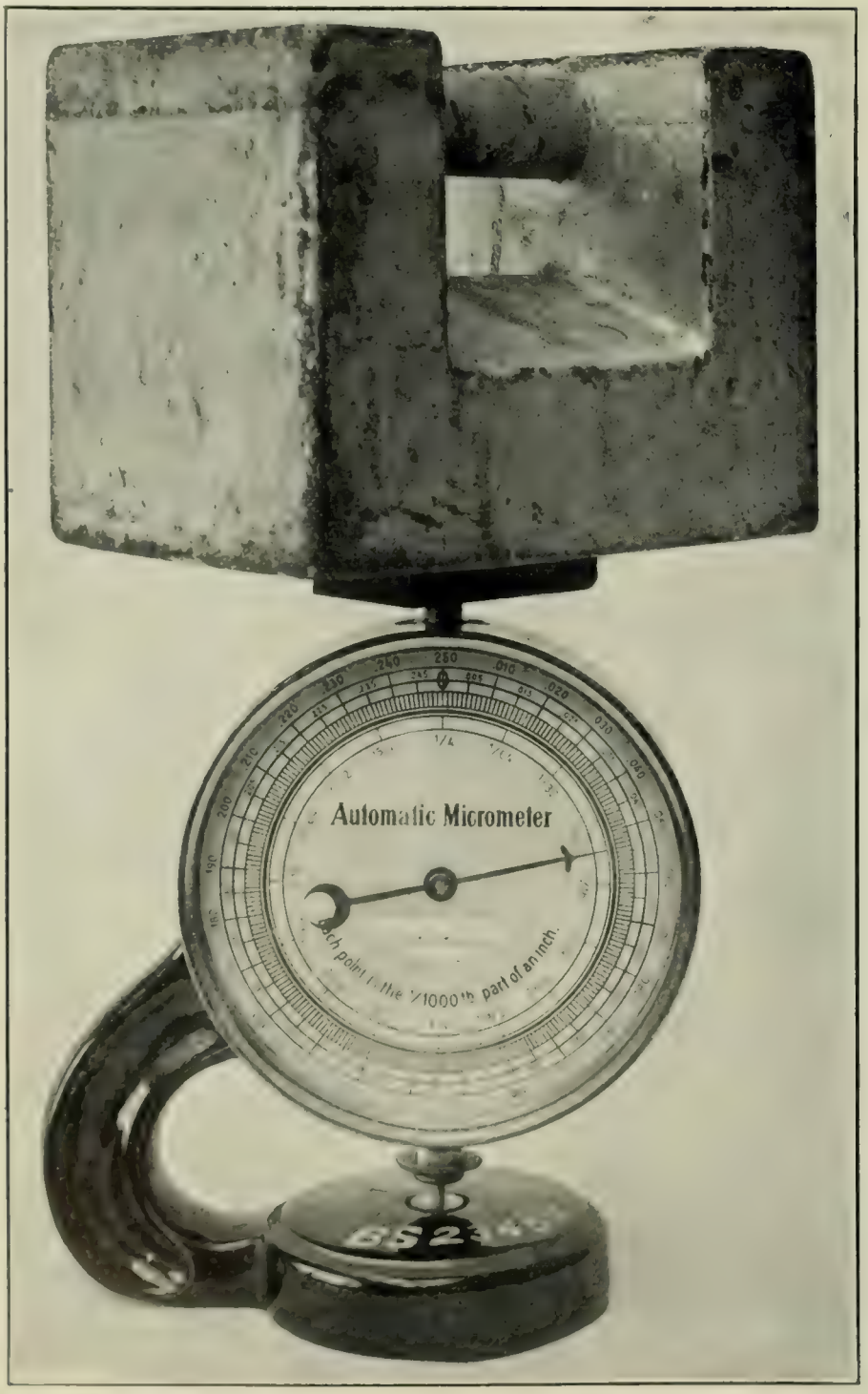


FIG. 21.—*Micrometer adapted to measure flow of amalgam*

the crushing load is applied as rapidly as possible the crushing strength always runs high.

Most amalgams, after setting 48 hours, will show crushing strength of over 32 000 pounds per square inch if crushed quickly, say in 3 minutes; but by applying a constant pressure of 3200 pounds, only one-tenth the previous crushing load, we found it possible to crush some of these same amalgams within 20 hours.

With these facts established it was decided to make comparative flow tests, beginning 2 hours after packing, and applying the approximate one-tenth load, namely, 3200 pounds per square inch.

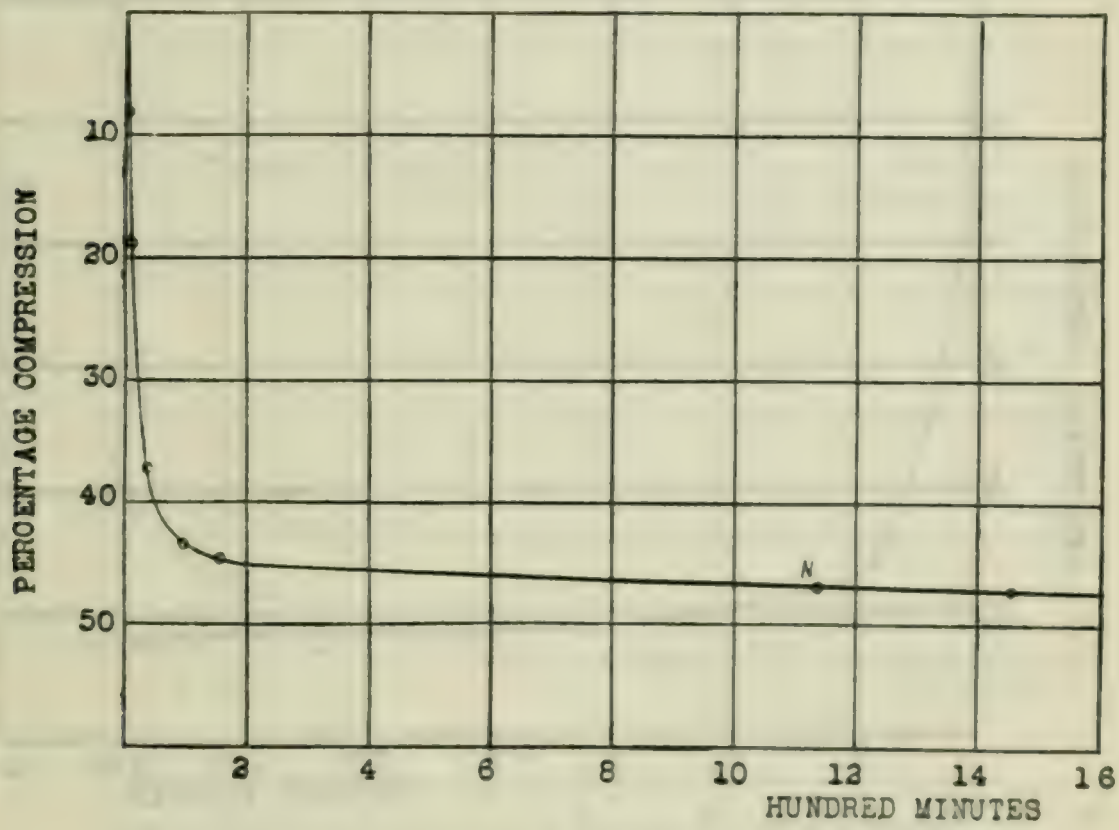


FIG. 22.—*Flow of amalgam; load applied two hours after packing*

The load was applied to a specimen 4 mm in diameter and about 8 mm long.

The apparatus used for the flow tests is shown in Fig. 21 and consists of a micrometer with a weight pan attached at the top of the upright rod or plunger. The two ends of the specimen are cut at right angles to the axis and placed between the jaws of the micrometer. As the amalgam is compressed by the weight applied at the top of the rod the indicator moves around the dial. The difference of readings gives the amount of compression or flow. An air cushion plunger incorporated in this micrometer

prevents injury to the instrument should the specimens fracture suddenly.

Changes in length are indicated on the dial. These are recorded as per cent change in total length. Figs. 22 to 25 are included to portray the average behavior of amalgams when subjected to this test.

Fig. 22 was plotted from data taken under the above conditions. Two hours after amalgamation and packing the specimen was placed in the compression micrometer and a pressure of 3200 pounds per square inch applied. In 30 minutes it was compressed

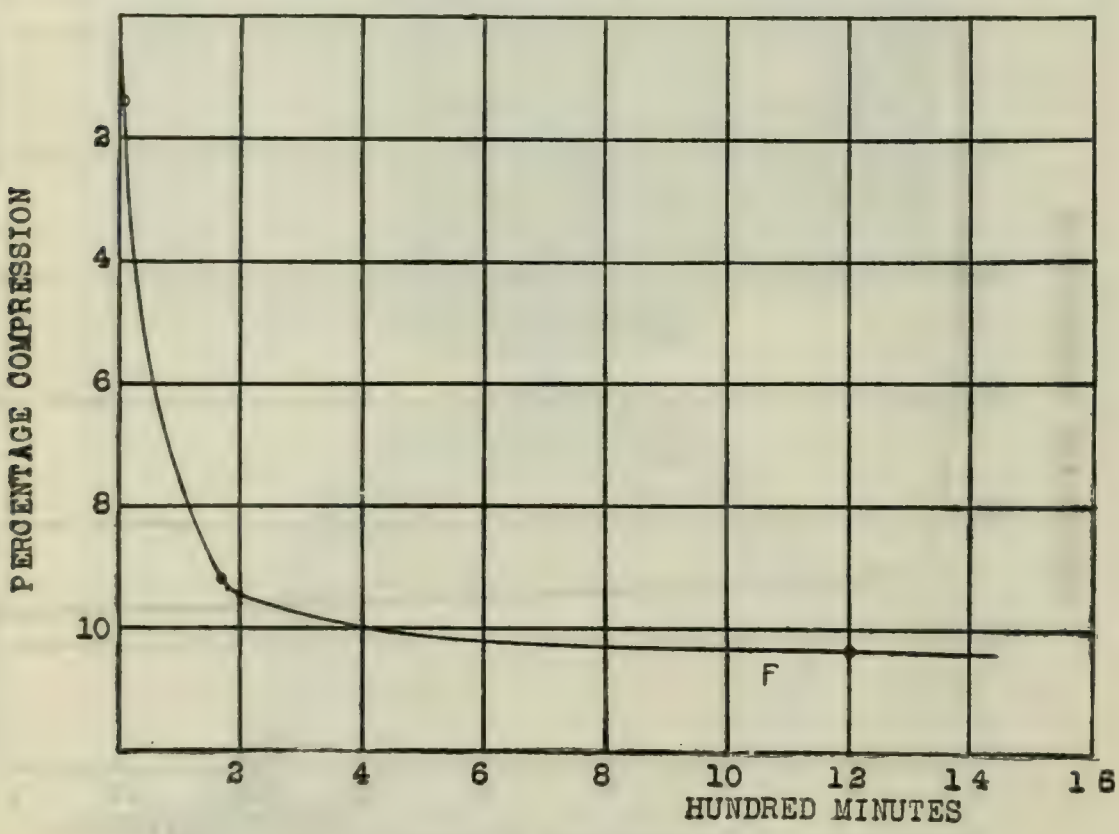


FIG. 23.—*Flow of amalgam; load applied two hours after packing*

40 per cent. This specimen did not flow materially after 10 hours, due to the fact that the cylinder had been ruptured and was spread over a much larger area, thus reducing the effective pressure per square inch.

There was a possibility of this apparent recovery in ability to resist flow being attributable to delayed crystallization (slow setting), so additional specimens were prepared and retained 48 hours before being subjected to the flow test. The same amalgam under this treatment was compressed 18 per cent and fractured after three days. (See Fig. 25*N*.)

Fig. 23 is plotted for another amalgam, compression started 2 hours after packing. This alloy was marked "Quick setting."

Fig. 24 (top) indicates the flow of a 5 per cent *Zn* amalgam and the curve at the bottom is for a nonzinc amalgam. The amalgams in Fig. 25 were not subjected to the one-tenth load until 48 hours after condensing. Amalgam *N* is the same as that used in Fig. 22.

Most amalgams will withstand this test remarkably well at 1 hour and some at 30 minutes after packing. The qualities producing failure seem to be inherent and permanent in the material (probably chemical compositions) and permit failures after 48 hours as readily as after 30 minutes; the so-called slow-setting or quick-setting qualities being difficult to interpret.

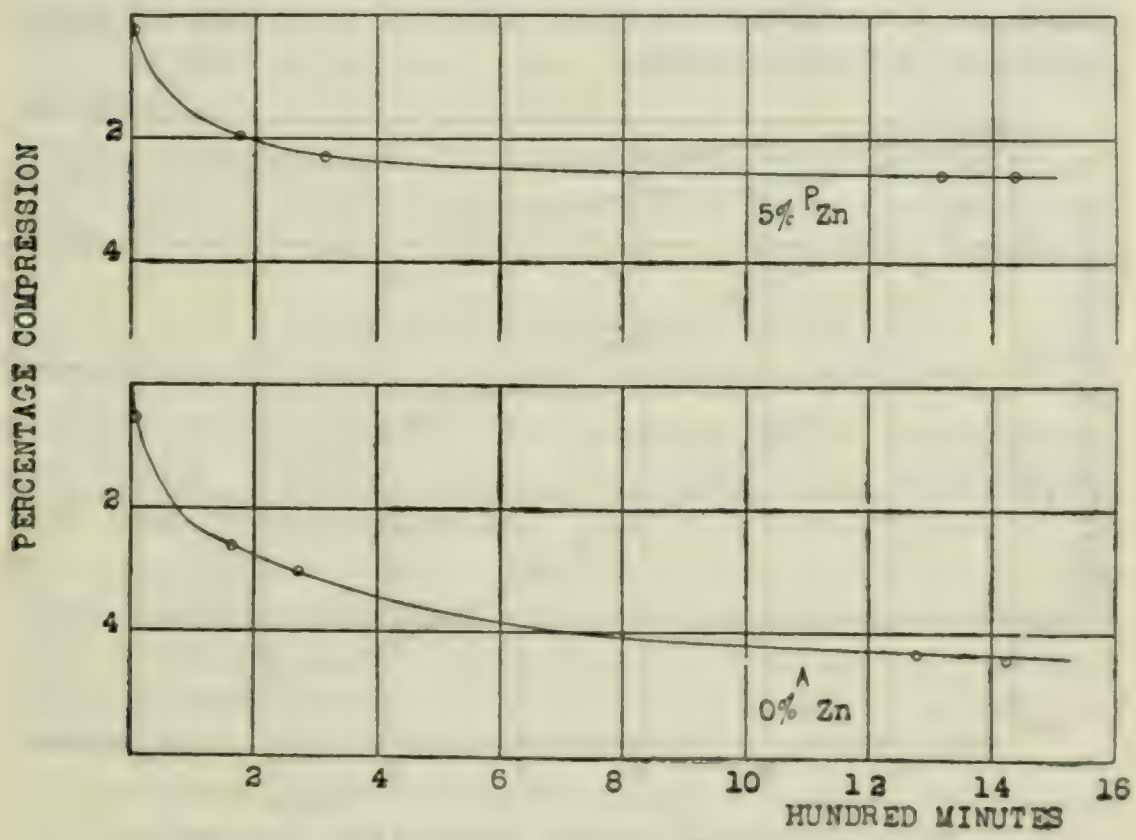


FIG. 24.—*Flow of amalgams; load applied two hours after packing*

The above may appear to be a new feature, but such is not the case, as it is simply a modification or improvement on the Black dynamometer in which a set of levers operating a dial hand is used to indicate the compression during the crushing tests. The constant, continuous load of one-tenth the crushing value is selected as appropriate for deciding upon the merits of an amalgam when used in a cavity such that it is required to furnish a contact point with an adjacent tooth or filling where constant pressure is applied. The permanence in shape and position of this contact point will eliminate later troubles and constant annoyances due to food par-

ticles which tend to wedge between the teeth. The possibilities of position changes are of importance and the inevitable upsetting of the amalgam tooth margins needs only mentioning to bring one to realize the gravity of such situations. The point of a tooth from an opposite jaw constantly striking an amalgam may apply an effective load of several thousand pounds per square inch even though the gross pressure is only a few pounds. The smallness of the area of contact has the effect of intensifying the impacts when considered in terms of pounds per square inch. The material is being treated in a manner very similar to that employed in battering the head of a rivet where light taps continued for a short time are quite sufficient to change the entire cylindrical end into a flat bur.

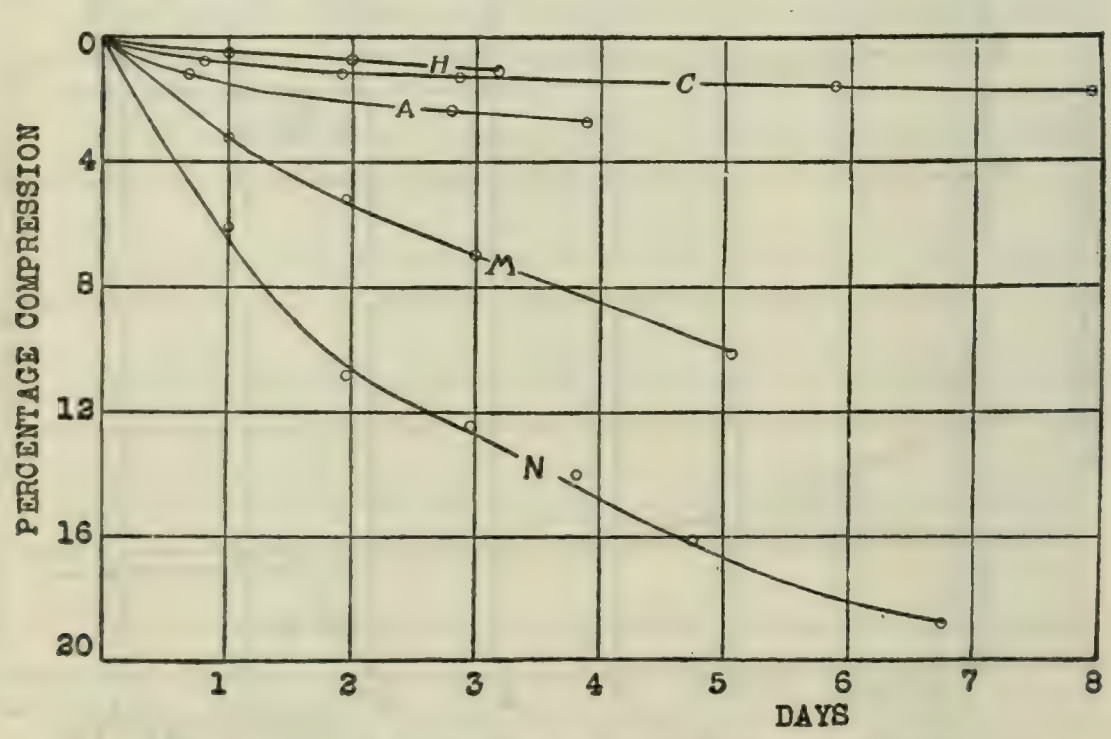


FIG. 25.—*Flow of amalgams; load applied 48 hours after packing*

## VII. CRUSHING STRENGTH

As previously stated crushing strengths have been found dependent upon the time occupied for the test. The tests included in this report were made as rapidly as convenient, using a specimen 6 mm in diameter and 10 to 12 mm long. While not of the size specified by the A. S. T. M. mentioned previously, they are a close approximation to the form. The preparation of specimens 1 inch in diameter and 2½ inches long would introduce factors and difficulties of trituration and condensation which are never encountered in practice, to say nothing of the enormous expense necessary to produce such quantities of alloy.

The regular testing machine equipment of the Bureau was used for these tests. The time required for each crush was about three minutes. Tests were made 14 days after amalgamation. All materials included in this test were made up according to the regular dental technique, in fact, extra specimens were made up by a practicing dentist for comparison and concordant results were found.

By mechanically packing the specimens under high pressure, immediately after amalgamation, it is possible to secure crushing tests of almost twice the values given in the table at the close.

The results of compressional tests are somewhat irregular, but no more so than those found by other observers. It is felt that the comparisons between alloys makes these data worth presenting.

Since these tests were for comparison and were made under similar conditions no extra precautions were taken to control temperature, which was constant at about 25° C, probably within 2°.

## VIII. BLACKENING OF HAND

This test consisted in mulling specimens in the hand two minutes after having first been amalgamated for one minute in the mortar. The hands were first washed, rinsed several times, and then dried to make sure that tests were comparable. A zero value indicates that no blackening was detectable; 10 represents a complete and dense black coat or film left in the palm. The values given are the average of several tests by different manipulators. In no case was there a variation of over two points, due to different tests or observers.

The authors will not attempt to pass on the merits of this test. The discoloration of the hand does not a priori imply a discoloration of the tooth tubuli. The free sulphides or combinations of foreign materials producing this blackening require further study to determine their true effect in amalgam usages.

## IX. CHEMICAL COMPOSITION

The chemical compositions vary from 45 to 69 per cent silver and from 0 to 5 per cent zinc, copper and tin making up the remainder.

For practically all alloys the claim of balance according to the G. V. Black standard is made, which can probably be interpreted to mean that the resultant filling should expand slightly, never contract, and after a few hours "lay still."

While absolutely exact percentages should produce exactly the same alloys if similarly treated, it is very probable that other factors enter which are far more significant; for example, a certain alloy triturated 3 minutes gave 5 microns expansion in 24 hours. This same alloy gave 15 microns contraction when triturated for 30 minutes. A similar behavior was found for other alloys. Overannealing while exposed to the air at 120° C for 2 hours in an electric oven produced little change in this chemical expansion or contraction, although it did render the alloy slow setting and of granular consistency while being mulled. Balancing an alloy then becomes meaningless unless proper instructions are given for time of trituration, etc.

In this investigation comparatively little interest was paid to the manufacture of alloys since the purpose of the research was to test the finished product. No effort was made to run a set of definite percentages of materials to recommend the proper proportions for a perfect alloy—the companies doubtless prefer to have this left as their field. The properties of cleanliness, size of cut, time of setting, working qualities, annealing, and the like must all be incorporated in the material and each manufacturer will endeavor to strike an average such that the alloy will contain a maximum of desirable qualities.

Certain desirable or undesirable properties are supposed to accompany excessive or deficient amounts of the constituent metals, for example, alloys of low percentages of silver are supposed to be deficient in strength, of poor working qualities, and slow setting; that is, tend to flow badly. These facts were verified qualitatively only. (See Table 3.)

High percentages of copper are said to produce discoloration—this of course should be or may have been settled by the dental profession. However, an amalgam made from an alloy containing 16 per cent copper was discolored when exposed to a weak solution of iodine, very much more than any of four others containing a lower amount of copper.

Zinc has long been considered a "disturbing" element. The claim is often made that zinc is "inadmissible," even in the smallest amounts, and that all amalgams containing zinc will "move." Since this movement is supposed to be cumulative and to extend over a period of years, it is impossible to furnish data extending over a period sufficiently large to be of decisive value.

A number of specimens have been prepared and are under observation. These have been divided into two groups, one of which is kept at room temperature, the other is subjected to temperature variations between zero and 50° C. At the end of the fourth month the first group had changed in length by values ranging from 0 to 0.2 per cent, one zinc amalgam showing the zero change, another zinc showing the 0.2 per cent change. The values obtained by averaging the changes of zincs against the nonzincs, disregarding signs, indicate a more nearly permanent state for the latter.

The group subjected to temperature variations (0 to 50° C) has suffered much greater changes. Here the average departures from initial length appear to favor the zinc amalgams, the average departure being 0.1 per cent, while the average departure for nonzinc amalgams is 0.2 per cent. The extremes of the former are 0.02 and 0.5 per cent and of the latter 0.06 and 0.4 per cent.

Manifestly no definite conclusions can be drawn from the comparison at this time. At a later date it will be possible to give more conclusive evidence bearing on this phase of the problem.

## X. ELECTRODE-POTENTIAL DETERMINATIONS

The normal calomel half cell and potentiometer was used in measuring the potentials. A description of this instrument may be found in any text book of physical chemistry. All values except the last are for the resultant amalgam using the alloys specified. A number of amalgams, ranging in values from 0 to 5 per cent zinc, were tested. These are given in Table 2. The potentials are expressed in terms of volts, electromotive force.

TABLE 2

| Alloy | Emf | Alloy | Emf |
|---|---|---|---|
| 0 per cent Zn | −0.54 | 1 per cent Zn | −0.52 |
| 0 per cent Zn (duplicate) | − .55 | 2 per cent Zn | − .52 |
| 0 per cent Zn, 16 per cent Cu | − .52 | 5 per cent Zn | − .51 |
| 0 per cent Zn, 16 per cent Cu (duplicate) | − .52 | Gold (metallic | + .002 |

No conclusive inferences are to be drawn from these although there seems to be little evidence of excessive contact emf effects due to the larger zinc content.

These tests seem to point toward a complete solution of the zinc (at least) by the mercury. This finding is in harmony with

the practice of giving zinc electrodes a surface amalgamation to prevent local action, due to impurities when placed in the solution of the electric cell.

**TABLE 3.—Comparison of Amalgams**

| Alloy | | Crushing strength in pounds per square inch | Per cent flow in 24 hours | Relative blackening | Setting changes, first 24 hours (all values in microns per centimeter) | | | Claims |
|---|---|---|---|---|---|---|---|---|
| Mark | Partial composition | | | | Maximum contraction | Maximum expansion | Final state | |
| A | Ag 68.... | 49 500 | 4.4 | 7 | 1.5 | 5.6 | + 4.3 | A correct material certified as to balance |
| | Zn 0..... | 51 550 | ..... | ..... | ..... | ..... | + 4.5 | |
| | | | | | | | + 2.2 | |
| B | Ag 67.... | 46 500 | 3.1 | 1 | 3.9 | 1.5 | + .5 | It is balanced, produces a white amalgam of great strength, free from slighest contraction, has a slight initial expansion never exceeding 3/10 000 inch, takes a high polish |
| | Zn 2..... | 40 300 | ..... | ..... | ..... | ..... | − 1.7 | |
| | | | | | | | − .2 | |
| C | Ag 68.... | 39 800 | 4.0 | 0 | .6 | 6.7 | + 5.2 | Made in accordance with the investigations of Dr. G. V. Black; is a balanced alloy. This is a perfect alloy in every respect, is age proof, an exact alloy, highest crushing strength, is the only chemically clean alloy made |
| | Zn 1..... | 38 200 | ..... | ..... | ..... | ..... | + 6.7 | |
| | | 44 200 | ..... | ..... | ..... | ..... | + 4.9 | |
| D | Ag 66.... | 39 950 | 3.4 | 0 | .8 | 5.5 | + 2.1 | |
| | Zn (1)... | 35 550 | ..... | ..... | ..... | ..... | + 2.6 | |
| | | | | | | | + 3.7 | |
| E | Ag 60.... | 41 950 | 9.1 | 4 | 9.2 | .0 | − 6.8 | White alloy |
| | Zn ( )... | 38 900 | ..... | ..... | ..... | ..... | − 5.7 | |
| | | | | | | | − 5.0 | |
| F | Ag 66.... | 49 500 | 10.4+ | 2 | 27.1 | .0 | −27.1 | A balanced alloy made after the approved formula of G. V. Black, M. D., D. D. S. |
| | Zn 1..... | 48 400 | ..... | ..... | ..... | ..... | −21.3 | |
| | | | | | | | −20.2 | |
| G | Ag 68.... | 47 250 | 5.0 | 4 | 3.5 | 1.7 | + .4 | Never changes color, contraction nil, expansion 1/20 000 |
| | Zn ½..... | 46 650 | ..... | ..... | ..... | ..... | − .3 | |
| | | | | | | | − 1.4 | |
| H | Ag 67.... | 40 750 | 3.7 | 1 | 4.1 | 4.3 | + 3.8 | Used by the U. S. Navy made after the Black formula |
| | Zn 1..... | 40 750 | ..... | ..... | ..... | ..... | + 3.5 | |
| | | | | | | | + .7 | |
| I | Ag 68.... | 38 700 | 4.3 | 1 | 7.7 | .0 | − 7.5 | Does not shrink, about 1/20 000 expansion takes place; a perfect, nonleaking amalgam can be the only result |
| | Zn ¾..... | 37 100 | ..... | ..... | ..... | ..... | − 6.5 | |
| J | Ag 67.... | 42 750 | 7.8 | 8 | 1.2 | 3.8 | + 2.5 | A balanced alloy, permanent whiteness, made by the Black method, contraction nil, expansion 1/20 000 |
| | Zn 1..... | 44 800 | ..... | ..... | ..... | ..... | + 2.4 | |
| | | | | | | | + 2.5 | |
| K | Ag 54.... | 41 550 | 9.6 | 8 | 2.4 | 4.9 | + 1.4 | Depended upon not to shrink or change form; insures against stained teeth and gutters around fillings |
| | Zn 0..... | 48 450 | ..... | ..... | ..... | ..... | + 3.9 | |
| | | | | | | | + 4.2 | |
| L | Ag 54.... | 33 600 | 5.3 | 4 | 2.1 | 3.2 | + 2.6 | Fillings do not shrink nor change form; has a fine white color which endures; can not shrink |
| | Zn 0..... | 38 700 | ..... | ..... | ..... | ..... | + 3.0 | |
| | | | | | | | + 2.1 | |
| M | Ag 54.... | 30 400 | 36.0 | 10 | 39.1 | .0 | −28.1 | No shrinkage, no discoloration, a tooth saver; any higher price can not buy a better alloy; an honest, efficient filling material; takes a high polish and keeps it |
| | Zn ½..... | 34 300 | ..... | ..... | ..... | ..... | ..... | |
| | | 30 300 | ..... | ..... | ..... | ..... | ..... | |
| N | Ag 45.... | 30 850 | 47.1 | 7 | 7.8 | .0 | − 3.8 | Nonshrinkage, nonexpansion, edge strength, retention of color |
| | Zn 2..... | 38 500 | ..... | ..... | ..... | ..... | ..... | |
| | | 30 000 | ..... | ..... | ..... | ..... | ..... | |
| O | Ag 67.... | 40 750 | 2.5 | 2 | 1.9 | .0 | − 1.9 | |
| | Zn 1¾.... | 34 000 | ..... | ..... | ..... | ..... | ..... | |
| P | Ag 60.... | 41 200 | 2.6 | 1 | 7.2 | .0 | − 4.5 | |
| | Zn 5..... | ..... | ..... | ..... | ..... | ..... | ..... | |

Table 3 gives a brief comparison of the more important qualities investigated. Some of these are readily verifiable by the interested dentist who is willing to spend the money necessary to purchase the alloys. Others require special apparatus or the services of a testing laboratory, for example, crushing strength and flow, while others require apparatus of such high precision that in addition to the apparatus it is essential to have the tests carried out by a person skilled in the use of such apparatus, for example, accurate determinations of expansion and contraction.

The claims tabulated are those made on the label of the package or in advertisements placed before the public in recent years.

It is a regrettable situation that individual practitioners will find it practically impossible to make complete tests on the materials supplied as balanced alloys to conform to methods of Dr. Black, or any formula or specification. However, it is felt that the manufacturers turning out products which are of a questionable value will welcome any move to place this work on a scientific basis, thus eliminating the necessity for lower standards often used in the fields where price is put before permanence.

There may possibly exist a place for the materials of questionable qualities—that is, tendency to flow excessively or to contract on setting—which necessitates their production and place in the market. If so, specific information should accompany each package, giving full details.

## XI. SUMMARY

A survey of the previous work on the physical properties of dental materials reveals a large amount of qualitative work on certain properties with instruments, the inherent errors or sensitiveness of which are comparable with the magnitude of the effect under investigation.

Many of the essential properties have not been considered and in some cases a careless interpretation of results has led to considerable confusion.

Recent work by Dr. Gray, of Milford, Del., with improved apparatus, has indicated the possibilities and importance of obtaining qualitative results on more of the properties. At the request of a branch of the Government the authors undertook such an investigation.

An inspection of the instruments in general use disclosed their lack of sensitivity and necessitated the construction and employment of more suitable apparatus.

Accuracy and efficiency recommended the use of the interferometer for determinations of thermal expansion and setting changes, since the necessary accuracy can be secured with the use of small specimens, the temperature of which is readily controlled.

For crushing strength determinations the calibrated testing machines of the Bureau were used. For the flow tests it was found desirable to select a special instrument. This instrument consists essentially of a precision dial micrometer equipped for applying constant, continuous pressures to specimens.

The electrode-potential measurements were made with the calomel half cell and potentiometer, which is standard apparatus for such measurements.

Careful chemical analyses were made to determine the constituents of the different alloys.

The results of the determinations of the properties tested, which are represented in the accompanying curves and tables, show the behavior of different alloys and the effects of different conditions and manipulations upon the same alloy.

Because of our lack of sufficient clinical experience we have not attempted to speculate on our data except under definite physical conditions, but have attempted to emphasize to the profession some of the important properties, together with a means of determining the same.

We are pleased to make the following acknowledgments of assistance:

Dr. H. D. Holler, Bureau of Standards, for measurements of electromotive force; Miss H. C. Baker and A. M. Weber, Bureau of Standards, for determining crushing strength of specimens; Mr. J. H. Scherrer, Bureau of Standards, for chemical analyses; R. L. Coleman, Bureau of Standards, for amalgamating numerous specimens, etc.; and to the following manufacturers cooperating: Atkinson Laboratories, L. D. Caulk Co., Cleveland Dental Co., J. M. Ney Co., and S. S. White Dental Manufacturing Co.

WASHINGTON, November 24, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

## No. 158

# A PECULIAR TYPE OF INTERCRYSTALLINE BRITTLENESS OF COPPER

BY

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1920

# A PECULIAR TYPE OF INTERCRYSTALLINE BRITTLENESS OF COPPER

By Henry S. Rawdon and S. C. Langdon

The following note describing the behavior of copper under rather unusual conditions is believed to be of considerable industrial importance as well as of scientific interest, and is offered here for its suggestiveness rather than as a complete study of the question. The examinations described were made in response to an inquiry addressed to the Bureau of Standards requesting information concerning the embrittlement of copper when heated in a molten salt bath (sodium chloride) for the purpose of cleaning it as well as for softening it. It is well known that metals may be rendered very brittle by electrolytic action in aqueous solutions, in all probability by the action of nascent hydrogen, and it was suspected that perhaps the embrittlement of the copper by means of the molten salt was produced in a somewhat similar manner.

It was found that the copper was in contact more or less with iron (or steel) while immersed in the molten salt. This came about through the use of an iron stirring rod occasionally, iron forceps for handling the pieces, and an iron pot for containing the fused salt. In the electrochemical potential series iron and copper stand some distance apart, copper being electronegative to the iron. Assuming that the two metals bear a similar relation to each other when immersed in a bath of molten salt as they do in an aqueous solution, they would be expected to form a "galvanic couple," the copper being the cathode. By this means the copper might be embrittled, as often happens in aqueous solutions by the action of the liberated hydrogen. In this case, however, the embrittlement must be attributed to some other agent than hydrogen.

To demonstrate how copper may be embrittled under these conditions, two small rods, one of copper and the other mild steel, approximately three-eighths inch diameter, were immersed

in a bath of sodium chloride which had been heated somewhat above its fusion point (melting point of sodium chloride, 819° C.) and an emf of approximately 6 volts from a storage battery was impressed upon the system. The copper was made the cathod and the action was continued for several minutes. When removed from the bath, cooled, and tested for brittleness by bending the specimen back and forth while clamped firmly at one end in a vise, the copper rod was found to be very brittle, as compared with a rod of the same length of the untreated copper tested in the same manner. In a similar set-up the copper was made the anode of the electrolytic cell and tested for brittleness in the same manner. In this case the copper proved to be as soft and tough as the original and to require practically the same number of bends to cause it to fracture. It showed no evidence of embrittlement.

Sections of the three rods were examined microscopically in the endeavor to show the cause of the pronounced difference in mechanical properties due to the treatment. The specimens were first plated with nickel, after which a thick layer of copper was deposited electrolytically. This was done so that when the rods were cut and polished for microscopic examination the edge would be protected and the structure of the surface metal could be examined readily up to the extreme edge.

The micrographs illustrate the structure of the material in the three conditions. Fig. 1 shows the copper of the rod used. Though not a hard-drawn rod, the final annealing which was given the metal during its manufacture was not sufficient to remove all evidence of distortion of structure due to cold work. The metal pitted rather badly upon etching, due to inclusions of oxide; the surface of the rod appears rather rough at the magnifications used (× 500) as compared with the same material after treatment in the fused salt.

Fig. 2 shows the copper rod after using it as the anode in the fused-salt electrolytic cell, the cathode being iron. The surface has been smoothed and cleaned so that the edge of the cross section is now an almost perfect arc of a circle. The structure is that of annealed copper, all evidence of cold working has been erased. The inclusions of cuprous oxide are still present but are uniformly distributed and the metal shows nothing in its structure suggestive of brittleness.

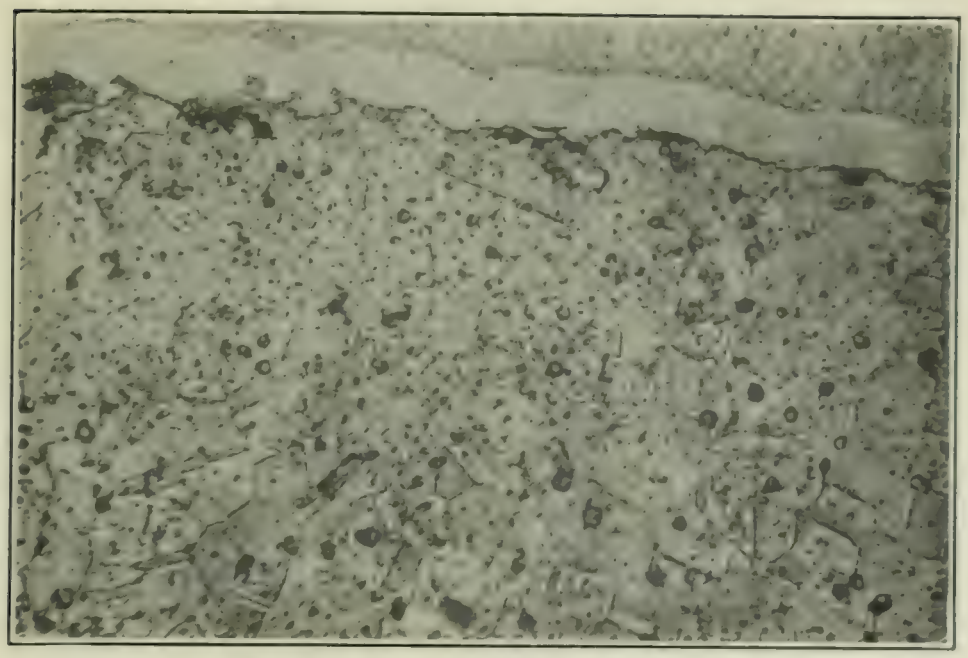
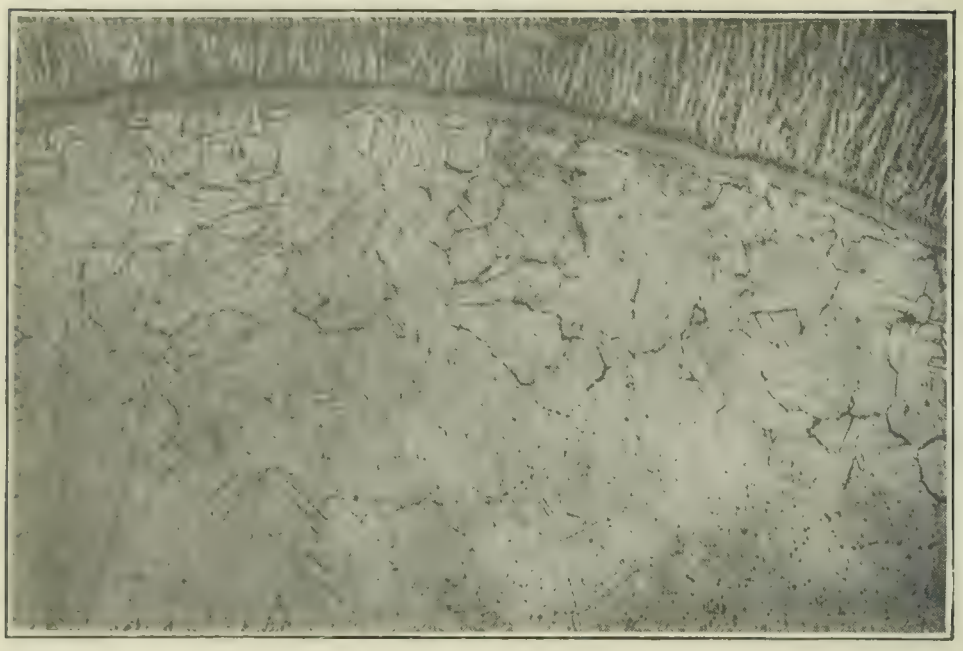


FIG. 1.—*Initial condition of copper rod*

The rod was sectioned transversely. The white band is the layer of nickel, which with the electrolytic copper outside it was used to protect the edge of the section during polishing. The dark spots represent inclusion of cuprous oxide. The etching fluid was concentrated ammonium hydroxide and hydrogen peroxide. ×500

FIG. 2.—*Copper used as anode in fused-salt electrolytic cell*

The high temperature increased the grain size considerably. The edge of the section of the rod has also been smoothed by the etching action of the fused salt. Etching fluid, concentrated ammonium hydroxide and hydrogen peroxide. ×150



(*a*) ×100

(*b*) ×500

FIG. 3.—*Copper used as cathode in fused-salt electrolytic cell*

The specimen has been slightly etched with the same reagent as in Figs. 1 and 2. A very marked intercrystalline attack of the surface metal occured in the fused-salt bath, by which the grain boundaries are very strongly marked. The surface of the metal was protected as in Figs. 1 and 2

Fig. 3, *a* and *b*, shows the copper rod after its use as the cathode. In Fig. 3, *a* (× 100) a well-defined surface layer is to be seen, in which the crystalline boundaries are very strongly defined. They are to be seen even before the metal is etched. Fig. 3, *b* shows the lightly etched specimen at a higher magnification; the intercrystalline or boundary markings are of an appreciable width and are not merely separations between the grains. The cuprous oxide inclusions are also to be seen distributed much the same as in the other specimens. They do not appear as conspicuous in this specimen as the others, since the metal was etched more lightly.

The probable explanation of embrittlement of the copper when it is made the cathode is that an appreciable amount of metallic sodium is formed by the electrolysis which immediately alloys with the copper. The most striking feature is the selective attack by which the metal of the grain boundaries is acted upon and the action progressed inwardly between the crystals instead of forming an alloy layer upon the outside of uniform thickness. The behavior of the specimen of Fig. 3 when subjected to the bend test is of interest in illustrating the effect of a relatively thin brittle skin upon the properties of a relatively much larger piece. The structure of the interior of the specimen shows no evidence of brittleness any more than does that of the rod used as anode, or the rod in its initial state. It may be assumed, therefore, that only a relatively very thin skin has been rendered brittle by the eletrolytic action; the properties of the entire rod have, however, been very profoundly changed.

WASHINGTON, November 22, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 159

# POROSITY AND VOLUME CHANGES OF CLAY FIRE BRICKS AT FURNACE TEMPERATURES

BY

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*Bureau of Standards*

APRIL 26, 1920

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1920

# POROSITY AND VOLUME CHANGES OF CLAY FIRE BRICKS AT FURNACE TEMPERATURES

By George A. Loomis

CONTENTS


| | | Page |
|---|---|---|
| I. | Introduction | 3 |
| | 1. General considerations regarding the testing of fire bricks | 3 |
| | 2. Measurement of refractoriness | 4 |
| | 3. Temperature-porosity changes as an indication of load-carrying ability | 4 |
| | 4. Object of present investigation | 5 |
| II. | Description of fire-brick tests already used | 6 |
| | 1. Chemical analysis | 6 |
| | 2. Softening point | 7 |
| | 3. Load test | 8 |
| | 4. Cold crushing test | 9 |
| | 5. Ball test | 9 |
| III. | Method of study of porosity and volume changes in connection with load tests and softening points | 10 |
| | 1. Determination of porosity and volume changes | 10 |
| | 2. Method of making load tests | 12 |
| | 3. Method of determining softening points | 13 |
| IV. | Results | 13 |
| V. | Discussion of results | 20 |
| VI. | Practical application of porosity and volume measurements of clay fire bricks | 27 |
| VII. | Summary | 28 |


## I. INTRODUCTION

### 1. GENERAL CONSIDERATIONS REGARDING THE TESTING OF FIRE BRICKS

The testing and classification of clay fire bricks is a subject which has received considerable attention in recent years, but which has not yet been worked out to any great degree of completeness. Failure to satisfactorily classify clay fire bricks has been due, in part, to the fact that clay refractories are used under such a variety of conditions. A fire brick which proves very satisfactory under certain conditions of use may not be able to fulfill the requirements for other uses. Fire bricks may be called upon to resist deformation under excessive, or very light, loads at high temperatures, to resist sudden changes in temperature, to with-

stand intrusion of slags or glasses, to resist abrasive action, and many other equally severe conditions. Of course, no brick could be expected to withstand all of these conditions perfectly, and it would be hardly fair to condemn the use of a brick for all purposes because of failure to withstand any one of these conditions. However, it is generally conceded that refractoriness is a primary requisite of a fire brick for general use; and other properties, such as ability to resist abrasion or the penetration of slags, may be said to be of secondary importance. Therefore, the question of the satisfactory evaluation of refractoriness has proved the main problem in the testing and classification of clay fire bricks.

### 2. MEASUREMENT OF REFRACTORINESS

In working out a satisfactory classification of fire bricks, based on refractoriness several tests for the measurement of this property have been put into more or less general use. Of these the three which have been used the most are, first, the chemical analysis, which gives a theoretical indication of refractoriness; second, the direct determination of the so-called softening point; and third, the determination by an actual load test of the ability of a fire brick to resist deformation under loads at high temperatures. These tests will be described more in detail later. Another test as a measurement of refractoriness, but which has not been used very extensively in the case of fire bricks, is the determination of porosity and volume changes on heating the bricks to different temperatures. A decrease in porosity and volume indicates the progress toward vitrification, and when these changes are plotted in the form of curves the slope of the curves shows the rate of vitrification. Overfiring is then indicated by an increase in porosity and by an increase in volume as the vesicular structure accompanying overfiring is developed. A classification of fire clays, based on porosity changes, was first suggested by Purdy,[1] who set the limits for the different grades of refractories, as shown by the curves in Fig. 1. The idea of measuring the refractoriness of a fire brick by its changes in porosity and volume is evidently a sound one.

### 3. TEMPERATURE-POROSITY CHANGES AS AN INDICATION OF LOAD-CARRYING ABILITY

The value of the determination of porosity and volume changes is all the more evident when it is realized that the degree of vitrification, as shown by the changes in porosity, also represents the

[1] Purdy, R. C., Bull. No. 9, Ill. Geol. Sur.

amount of softening which must necessarily take place in the process of vitrification. Marked softening of the mass of the brick means decreased resistance to deformation. In other words, the changes in porosity may be said to bear some relation to the resistance to deformation of a brick under load at high temperatures.

### 4. OBJECT OF PRESENT INVESTIGATION

From the above considerations it is evident that the determination of the porosity and volume changes is very valuable in the study of the fundamental properties of clay fire bricks, and it is only by a better knowledge of the fundamental properties that a

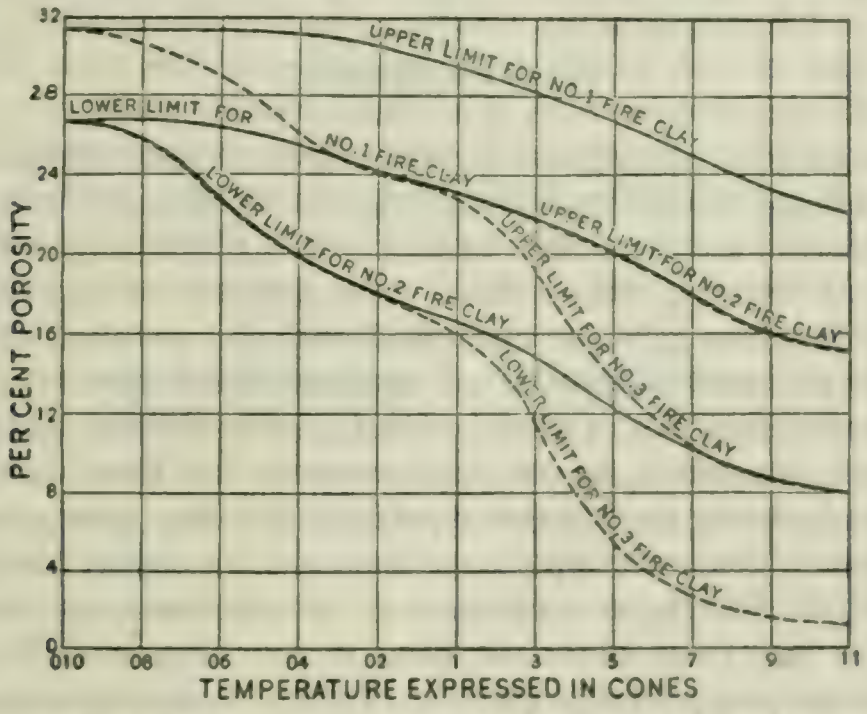


FIG. 1.—*Diagram showing Purdy's classification of fire clays*

completely satisfactory classification of fire bricks can be worked out. Therefore, the present investigation was undertaken in order to study the fundamental properties of clay fire bricks by a comparison of their changes in porosity and volume on heating to different temperatures with the results of a specific load test and with the so-called softening points.

Preliminary work on this investigation was first undertaken under the direction of G. H. Brown when connected with this Bureau. It was afterwards decided to take up the investigation on a larger scale, with the cooperation of the Refractories Manufacturers' Association, which kindly furnished samples of a greater number of brands of fire bricks for the tests, and likewise in the interest of the American Gas Institute.

## II. DESCRIPTION OF FIRE-BRICK TESTS ALREADY USED

Before taking up the details of the present investigation it is well to describe and discuss briefly the most noteworthy tests which are being used in determining the value of clay fire bricks, including the tests which have been mentioned already.

### 1. CHEMICAL ANALYSIS

The chemical analysis has been used to quite an extent in the study of the fundamental properties of fire bricks and is of considerable value, not only in this regard but also in explaining the causes of failure in use. The chemical analysis serves as an indication of refractoriness by showing the degree of purity of the clay. Clay of the purest type possible—that is, pure kaolin—has a softening temperature, or so-called melting point, of 1740° C.[2] This purest form of clay has a composition corresponding to that of the mineral kaolinite, being composed of 46.3 per cent silica, 39.8 per cent alumina, and 13.9 per cent chemically combined water. In burning, this chemical water is driven off and the composition becomes 53.8 per cent silica and 46.2 per cent alumina. Clay of this composition is of comparatively rare occurence, owing to the presence in most cases of quartz, feldspar, magnesia, lime, and iron oxide, in varying amounts, and these behave as fluxes in lowering the softening point of the clay to a greater or less extent. Some attempts have been made to apply the chemical analysis directly as a measure of refractoriness by means of formulas, but these have not been in any degree satisfactory. The determination of the amount of these fluxes by a chemical analysis, may, however, be considered as an aid in determining the refractoriness of the clay, as well as serving in some measure to explain the failures of clay fire bricks in use.

A classification of fire bricks based on the chemical analysis has been proposed [3] which fixes the limit for the permissible amount of fluxes for No. 1 grade bricks. According to this classification, the total amount of fluxes must not exceed 0.22 molecular equivalents. This expression for the amount of fluxes is a part of the empirical formula commonly used in the study of ceramic bodies. This is calculated from the chemical analysis by dividing the respective percentages by the molecular weights of the oxides and then dividing each value obtained by the value for

[2] B. S. Technologic Paper No. 10.

[3] B. S. Technologic Paper No. 7.

the alumina. The values for the various fluxes are then summed up, and the formula obtained is of the type x, $SiO_2$. 1 $Al_2O_3$.yRO. In this formula, determined for fire bricks, the RO equivalent must not exceed 0.22 for the No. 1 fire bricks, according to the suggested classification. In the case of the siliceous clay brick (say 65 per cent or more of silica) the permissible amount of fluxes is considerably less since the fluxes are more effective upon siliceous material. It is quite evident, then, that the chemical analysis is of some value in studying the causes of failure of refractories. However, there are physical tests which require less time to perform than the chemical analysis, and yet indicate much more satisfactorily the value of a fire brick in a practical manner.

### 2. SOFTENING POINT

The determination of the so-called softening point is one of the most widely used tests for fire bricks and is generally considered a reliable indication of the refractoriness of the material. In determining the softening point, small tetrahedra of the size of the well known Orton standard higher pyrometric cones, are molded from a portion of the brick ground to pass about an 80-mesh screen, and mixed with a gum-tragacanth solution to serve as a temporary bond. These are then set in a suitable plaque of refractory clay material beside a series of standard pyrometric cones and heated in a carbon-resistance electric furnace, or a small pot furnace heated with a gas-blast burner of the Fletcher type. The softening point is determined by the point at which the test cone deforms to the extent that the tip is on a level with the base or the cone has swelled excessively. Results are expressed in terms of the standard cone which has deformed to the same extent. Temperatures are not usually considered since it is a well-known fact that the bending of the standard cones is affected by the rate of heating. However, very good comparative results are obtained by limiting the time of firing on such a test to an hour and a half or two hours.

In classifying fire bricks according to the softening point cone 30 is usually considered the lowest value for No. 1 grade, cones 30 to 28 for No. 2, and cones 28 to 26 for No. 3 grade. This classification is, no doubt, a proper one, but, at the same time, it quite often proves misleading, in so far that the bricks with a higher softening point—cone 32 or above—sometimes fail to withstand practical conditions of load and temperature while

siliceous bricks, low in fluxes, with a softening point as low as cone 29, generally stand up well under heavy loads at fairly high temperatures. This is explained by the fact that siliceous bricks remain quite rigid to within about 100° C of their softening point, while the brick lower in silica softens through a longer range, Then, too, the softening-point determination is misleading in the case of bricks made from a coarse mixture of very refractory nonplastic clay (flint clay) with an inferior bond clay. The comparatively fine grinding necessary to molding the cones brings about a more intimate mixture of the material, so that the refractoriness is raised. This objectionable feature of the softening-point test is sometimes overcome by using a chip of the original brick cut on a carborundum wheel to the form and size of the standard cones. This, however, is often a difficult task and is practically impossible in the case of a very coarse, friable material, to say nothing of the variation in the results from not obtaining an average sample from so small a specimen.

### 3. LOAD TEST

What is known as the standardized load test was first used by this Bureau in an investigation of clay refractories. This test has proved the most practical and surest means of determining the behavior of fire bricks in use under high loads and temperatures. The test is generally performed upon a brick of standard size and shape placed on end in a specially designed furnace of about 20 by 20 by 20 inches, internal dimensions. The load is applied to the brick longitudinally through a suitable opening in the top of the kiln by means of a highly refractory column, on which rests a horizontal beam. On the furnace used by the Bureau this beam rests upon a knife-edge on the column and acts as a lever fastened and adjustable at one end to keep it level, and the load is applied at the other end. On a later type of load-test furnace the beam is balanced by applying an equal load on both ends, and no knife-edge is used. The firing, in the case of the Bureau's furnace, is done by means of eight Fletcher gas-blast burners, two on each side and four in front. In conducting this test the temperature is raised at a specified rate to the maximum temperature, which is held for one and a half hours. It has been found that 1350° C is the most suitable maximum temperature in testing first-grade fire bricks. A load of 40 pounds per square inch has been used, although this is rather severe, and one of 25 pounds per square inch is believed a fairer test for No. 1 bricks.

Although there are no standard specifications for clay fire bricks as yet, one-half inch contraction in length of a 9-inch brick is considered the permissible limit for a No. 1 refractory with a load of 40 pounds per square inch at 1350° C. All clay fire bricks which have not deformed more than one-half inch in such a test have proved very satisfactory in use under average loads at average furnace temperatures. Hence there seems to be no doubt whatever of the practical value of the load test. It may be a little too severe in rejecting bricks which might prove satisfactory in use, but this fault is easily remedied by decreasing the load applied.

### 4. COLD CRUSHING TEST

This test is a rather valuable one in eliminating unsatisfactory bricks from consideration for use under loads at high temperatures without taking time for the load test at furnace temperatures. Obviously a refractory possesses but a small part of its cold crushing strength at a temperature of 1350° C, and if a brick has a low crushing strength when cold it is almost certain to fail in a load test at 1350° C. It has been found that a cold crushing strength of 1000 pounds per square inch, when the brick is tested on end, is about the lowest permissible value in this regard.

### 5. BALL TEST

A special form of load test called the ball test has been put into use by Dr. J. S. Unger and C. E. Nesbitt, of the Carnegie Steel Co.[4] This test was devised in attempting to find a substitute for the regular load test, which could be performed on a larger number of bricks in a short time. It is claimed that results compare favorably with those of the regular load test. The test is made by heating bricks to 1350° C for one hour in a furnace, drawing them out quickly and laying them on their side under a long lever in such a manner that a 2-inch iron ball placed on the brick under the lever is depressed into the face as increasing pressure is applied to the lever. A certain load is applied which is gradually brought up to a maximum in about five minutes. The depression made by the ball is measured in inches. The proper load to give a depression comparable to the contraction in a regular load test was determined by experiment. There is no doubt that such a test can be made on a number of bricks in much less time than is required by the regular load test. How-

[4] C. E. Nesbitt and M. L. Bell, Proc. Am. Soc. for Testing Materials, 19, p. 369; 1916.

ever, there is some objection to it as a regular test for fire bricks on the ground that cooling takes place sufficiently during the test to influence the results. Then, too, the portion of the brick receiving the pressure is a small part of the whole brick, and the results are apt to be affected by small local defects in the structure of the brick.

The special tests of fire bricks, such as the determination of the resistance to slagging action, the resistance to impact and abrasion, and the test of ability to withstand sudden temperature changes, have little or no connection with the present investigation and need not be described here. [5]

## III. METHOD OF STUDY OF POROSITY AND VOLUME CHANGES IN CONNECTION WITH LOAD TESTS AND SOFTENING POINTS

### 1. DETERMINATION OF POROSITY AND VOLUME CHANGES

Taking up the details of the present investigation, the porosity and volume changes of the fire bricks, for comparison with the results of load tests and softening points were determined in the following manner: Specimens of each brand of fire brick were cut with a broad chisel into briquets, approximately 2½ by 1¼ by 1¼ inches in size, squared up somewhat on a grinding wheel, and suitably marked with cobalt paint (made by mixing powdered cobalt oxide, 1 part, and kaolin, 3 parts, in water). Six briquets were cut for each brand. A neater method of cutting the specimens would have been to use a carborundrum cutting wheel. However, the method used was quicker and equally as good except for the appearance of the specimens.

The initial porosity was then determined on two of these small specimens from each brand by first weighing the specimens to 0.10 gm after drying at 110° C and then determining the wet weight and the suspended weight after saturating in boiling water under a partial vacuum, represented by a 24-inch mercury column, for four hours. The per cent porosity was then determined from the Purdy formula:

$$\frac{\text{Wet weight} - \text{dry weight}}{\text{Wet weight} - \text{suspended weight}} \times 100 = \text{per cent porosity.}$$

The volume of the six briquets of each brand was then accurately determined in a volumenometer of the Seger type after

[5] For description of these special tests see Nesbitt and Bell, Practical Methods for Testing Refractory Fire Bricks, Proc. of Am. Soc. for Testing Materials, 16, p. 349; Brown, Method of Testing Corrosive Action of Slags, Trans. Am. Ceram. Soc., 18, p. 277.

soaking the specimens in oil. Duplicate determinations of each volume were made to obtain a check within 0.2 cc.

The six briquets of each brand were then set for reburning in a muffle in a test kiln in such a manner that a specimen for each brand could be drawn at regular intervals in the process of firing. Space was left between each set of draws and between individual piles to allow the equal heating of all briquets. A set of pyrometric cones and a thermocouple in a porcelain protecting tube were placed inside the muffle beside the briquets. With this arrangement the size of the muffle permitted the burning of 84 specimens or 14 brands at one time.

In burning the briquets, the temperature was brought rapidly up to 250–300° C and held for three or four hours in order to vaporize the oil in the briquets without igniting. Overnight the temperature was brought up to 800° C, this being the highest temperature that could be attained on this kiln without compressed air, which was not usually available at night. From 800° C the temperature was raised rapidly to 1200° C. The firing was then conducted at the rate of 30° C per hour from 1200 to 1500° C. The draws were made at 50° C intervals between 1250 and 1500° C and were cooled slowly by covering with hot sand in a suitable container.

The deformation of the standard cones as observed during the firing of the briquets was as follows:

Cone 13 down at 1350° C.
Cone 15 down at 1450° C.
Cone 17 down at 1500° C.
Cone 18 half down at 1500° C.

As usual, the cones were considered down when the tip was on a level with the base. It may be well to note here that cones, when used in a burn of this kind, are retarded slightly owing to the cooling unavoidably given them in making draws.

After the burning of the briquets the porosity of each was determined by the same method used in determining the initial porosities. It may be said in regard to the method of soaking the specimens that placing them in boiling water under a partial vacuum for four hours gave more consistent results than the usual method of simply boiling in water. It was found that results could be checked exactly on the same specimen by the vacuum method, whereas results by the boiling test alone were found to be sometimes as much as three points lower than by the vacuum method.

The final volumes of the briquets were determined in the volumenometer in the same manner as the initial volumes, checking

duplicate determinations on the same briquets to 0.2 cc. The volume change was computed in terms of the initial volume. The volume changes and porosities at the different temperatures were plotted in the form of curves for each brand of brick.

### 2. METHOD OF MAKING LOAD TEST

The regular load test was made on a full-sized specimen of each brand (standard-size bricks used), employing for an hour and a half a load of 40 pounds per square inch at a temperature of 1350° C The load of 40 pounds per square inch was considered best for testing first-grade fire bricks at the time the tests were made.

The kiln used for the load test was the one which has already been described.[6] Special care was used during these tests to keep the beam level at all times to prevent eccentric loading on the specimen. The usual rate of firing up to 1350° C was followed. It is given in Table 1.

TABLE 1.—Schedule of Firing in Load Test

| Time | | Temperature, °C | Time | | Temperature, °C | Time | | Temperature, °C |
|---|---|---|---|---|---|---|---|---|
| Hours | Minutes | | Hours | Minutes | | Hours | Minutes | |
| | 15 | 200 | 1 | 45 | 960 | 3 | 15 | 1240 |
| | 30 | 370 | 2 | ..... | 1020 | 3 | 30 | 1270 |
| | 45 | 520 | 2 | 15 | 1070 | 3 | 45 | 1300 |
| 1 | ..... | 670 | 2 | 30 | 1120 | 4 | ..... | 1320 |
| 1 | 15 | 800 | 2 | 45 | 1160 | 4 | 15 | 1340 |
| 1 | 30 | 880 | 3 | ..... | 1200 | 4 | 30 | [a]1350 |

[a] 1350° C held for an hour and a half.

The thermocouple used in measuring the temperature was placed within one-half inch of the bricks in a porcelain protecting tube. Cones were also placed close to the bricks as a check on the firing, although couples and instruments used in this test and for the porosity determinations were from time to time calibrated against standards to insure accuracy in measuring temperatures.

When the investigation was first started, the plan was to make duplicate determinations of the load test and to take the average result for comparison with the results of the porosity and volume-change determinations. However, the variation in initial porosity on different specimens of the same brand of bricks is sometimes quite considerable, due in most cases to a difference in burning in manufacture. It was therefore, decided to determine the initial

[6] B. S. Technologic Paper No. 7.

porosity on several of the full-sized bricks of each brand in the same manner as was done with the briquets and to use the brick for the load test which was found to have the nearest porosity corresponding to that of the briquets used in the other test. By so doing, it seemed that a good comparison of results of the load test with those of the porosity and volume-change determination could be made without making duplicate determinations of the load test on each brand. Under the circumstances, it did not seem worth while to take the time for more than one load test on each brand, considering the large number of brands tested.

### 3. METHOD OF DETERMINING SOFTENING POINTS

The softening-point determinations were made by grinding up portions of the bricks to pass a 60-mesh screen and molding with gum tragacanth into cones as nearly as possible the exact size of the Orton higher-pyrometric cones. These were set in a plaque of suitable refractory clay material with a series of pyrometric cones in the usual manner of determining softening points and fired in a small pot furnace, using a Fletcher blast burner with natural gas and compressed air. The time of firing on each test was limited to an hour and a half to two hours. The softening point was determined by the point at which the cones bent in the prescribed manner and the result expressed in terms of the corresponding standard cone. Duplicate determinations of the softening point were made on two bricks of each brand. Practically all of the results agreed within one-fourth of a cone and in no case did duplicate determinations on two bricks differ more than one-half cone.

## IV. RESULTS

The results of the determinations of the changes in porosity and volume, the load tests, and the softening points are given in Tables 2 and 3. The names of the brands are not given for obvious reasons, although the districts where they are made are indicated. The method of manufacture indicated in Table 2, was learned through information furnished by the makers. A general idea of the nature of the clays used, as explained by the manufacturer, is also indicated. Such information was not available in some cases, The bricks indicated as being handmade were hand molded and hand re-pressed; the stiff-mud bricks were made by a steam press or auger machine and power re-pressed, in accordance with common practice by the two methods. A great majority of the bricks in-

dicated as being made from a mixture of clays were made from the hard, highly refractory, nonplastic clays known as flint clays, bonded with a less-refractory, plastic clay, this being a common practice in the manufacture of clay fire bricks, especially in Pennsylvania.

The porosities and volume changes at the temperatures shown in the tables were taken from curves plotted accurately according to the actual temperatures at which the draws were made. The results of the load tests, given in Table 3, are expressed both in inches and in per cent of contraction figured upon the original length.

## TABLE 2.—Results of Tests of Fire Bricks Investigated

[Porosity and volume changes up to 1400° C. Other results are given in Table 3]

| Laboratory No. of brand | District where made | Process of manufacture | Per cent initial porosity of briquets | Per cent initial porosity of brick used in load test | Per cent porosity at 1300° C | Per cent volume change at 1300° C | Per cent porosity at 1350° C | Per cent volume change at 1350° C | Per cent porosity at 1400° C | Per cent volume change at 1400° C |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Pennsylvania | Stiff mud, using mixture of clays | 14.24 | (a) | 13.10 | 0.00 | 12.25 | +0.10 | 10.50 | +1.00 |
| 2 | do | Soft-mud machine, using mixture of some flint clay with plastic | 23.65 | (a) | 17.20 | −1.50 | 16.50 | + .75 | 16.95 | +6.65 |
| 3 | do | Soft-mud machine, using one clay | 22.80 | (a) | 16.35 | −2.35 | 14.40 | − .70 | 14.60 | +5.50 |
| 4 | do | Handmade, using mixture of clays | 23.15 | (a) | 22.90 | − .30 | 22.50 | + .10 | 21.95 | .00 |
| 5 | do | Handmade, using mixture of flint clay with plastic | 21.28 | (a) | 20.00 | .00 | 19.15 | + .30 | 17.55 | +1.30 |
| 6 | Maryland | Stiff mud, using mixture of flint clay with plastic | 24.46 | (a) | ..... | ..... | 20.50 | −3.10 | 18.00 | −2.95 |
| 7 | do | Handmade, using mixture of flint clay with plastic | 26.05 | (a) | 13.80 | −7.80 | 13.25 | −6.30 | 19.25 | +6.75 |
| 8 | do | Stiff mud, using mixture of flint clay with plastic | 22.95 | (a) | 11.65 | −7.00 | 12.25 | −5.00 | 16.45 | +2.50 |
| 9 | do | Handmade, using mixture of flint clay with plastic | 26.82 | (a) | 25.25 | .00 | 24.25 | .00 | 23.15 | − .15 |
| 10 | do | do | 30.00 | (a) | 16.75 | −9.15 | 16.10 | −7.15 | 16.10 | −3.25 |
| 11 | Missouri | Stiff mud | 18.03 | (a) | 17.45 | .00 | 16.15 | − .40 | 15.00 | − .35 |
| 12 | do | do | 19.50 | (a) | 18.40 | − .25 | 16.50 | −1.00 | 14.10 | −2.60 |
| 13 | do | do | 14.15 | (a) | 14.00 | − .05 | 13.50 | − .10 | 13.20 | −1.00 |
| 14 | do | Dry pressed | 16.33 | (a) | 16.15 | .00 | 15.70 | .00 | 13.75 | − .90 |
| 15 | Pennsylvania | Soft-mud machine, using one clay | 16.83 | (a) | 15.80 | .00 | 15.50 | .00 | 15.00 | .00 |
| 16 | do | Soft-mud machine, using mixture of clays | 21.67 | (a) | 20.20 | − .45 | 19.00 | −1.00 | 17.10 | − .60 |
| 17 | Kentucky | Stiff mud, using mixture of plastic and hard-soft clays | 12.40 | (a) | 10.90 | .00 | 9.40 | − .35 | 8.50 | + .25 |
| 18 | Colorado | Dry press, using two plastic clays | 25.32 | (a) | 25.15 | − .20 | 25.20 | .00 | 25.60 | + .30 |
| 19 | do | Stiff mud, using mixture of plastic and flint clay | 26.65 | (a) | 26.50 | .00 | 26.25 | − .25 | 25.90 | − .40 |
| 20 | do | Handmade, using mixture of clays | 25.60 | (a) | 25.30 | − .25 | 25.50 | − .40 | 25.65 | − .40 |
| 21 | do | do | 24.22 | (a) | 22.90 | − .15 | 23.40 | − .30 | 24.15 | − .40 |
| 22 | do | Stiff mud, using mixture of clays | 23.07 | (a) | 22.70 | − .25 | 22.35 | − .35 | 22.40 | − .75 |
| 23 | do | Stiff mud, using mixture | 19.08 | (a) | 18.75 | + .20 | 18.05 | + .30 | 17.80 | − .10 |

[a] Not determined.

## TABLE 2.—Results of Tests of Fire Bricks Investigated—Continued

[Porosity and volume changes up to 1400° C. Other results are given in Table 3]

| Laboratory No. of brand | District where made | Process of manufacture | Per cent initial porosity of briquets | Per cent initial porosity of brick used in load test | Per cent porosity at 1300° C | Per cent volume change at 1300° C | Per cent porosity at 1350° C | Per cent volume change at 1350° C | Per cent porosity at 1400° C | Per cent volume change at 1400° C |
|---|---|---|---|---|---|---|---|---|---|---|
| 24 | Pennsylvania | Dry pressed, using one clay | 19.54 | 16.20 | 18.90 | + 0.25 | 19.15 | +0.10 | 18.50 | + 0.25 |
| 25 | do | Handmade, mixture of plastic and flint clay | 19.95 | 19.22 | 20.15 | .00 | 19.25 | − .30 | 18.75 | − .45 |
| 26 | Maryland | Stiff mud, using single clay | 13.44 | 14.90 | 10.60 | − .75 | 8.60 | − .30 | 7.00 | + .10 |
| 27 | do | Handmade, using mixture of clays | 24.55 | ..... | 20.95 | − 1.15 | 21.00 | +1.00 | 21.00 | + 3.20 |
| 28 | do | do | 27.86 | 25.85 | 24.95 | − 1.60 | 22.25 | −2.85 | 20.50 | − .70 |
| 29 | do | Stiff mud, using mixture of clays | 21.10 | ..... | 18.67 | − 1.40 | 14.65 | −3.65 | 13.30 | − 3.15 |
| 30 | Pennsylvania | Handmade, using mixture of clays | 20.78 | 21.30 | 19.30 | + .26 | 16.25 | + .40 | 15.85 | + 1.60 |
| 31 | do | do | 23.63 | 22.00 | 22.25 | − .25 | 19.85 | − .75 | 18.60 | + .25 |
| 32 | do | Handmade, using mixture of plastic and flint clays | 23.33 | 24.90 | 21.65 | + .15 | 21.90 | +1.60 | 19.45 | + 3.30 |
| 33 | Ohio | Stiff mud, using single clay | 17.95 | 15.98 | 14.95 | − 1.65 | 10.80 | −4.15 | 9.00 | − 3.95 |
| 34 | do | Handmade, using mixture of plastic and flint clays | 25.98 | 26.40 | 19.75 | − 3.55 | 19.70 | −3.08 | 18.35 | − 3.70 |
| 35 | do | Handmade, using mixture of hard-soft and plastic clays | 22.13 | 23.10 | 18.90 | − .15 | 16.65 | −1.25 | 14.70 | − .74 |
| 36 | do | Dry pressed, using one clay | 21.23 | 23.60 | 17.95 | − .85 | 18.05 | + .90 | 15.45 | + 2.05 |
| 37 | do | Handmade, using one clay | 26.77 | 25.20 | 10.60 | −12.90 | 21.15 | +1.60 | 27.65 | +12.95 |
| 38 | do | Handmade, using mixture of plastic and flint clays | 30.36 | 30.20 | 27.40 | − 2.85 | 25.65 | −3.95 | 23.55 | − 5.45 |
| 39 | do | do | 30.10 | 28.00 | 28.70 | .00 | 28.30 | − .40 | 26.45 | − 3.05 |
| 40 | Pennsylvania | Handmade, using mixture of clays | 23.98 | 20.05 | 16.50 | + .50 | 15.00 | +1.55 | 14.40 | + 3.50 |
| 41 | do | do | 24.07 | 23.05 | 21.30 | − 1.50 | 20.50 | −1.05 | 19.00 | − .35 |
| 42 | do | do | 21.66 | 23.90 | 21.50 | − .65 | 20.50 | −1.10 | 17.75 | + .30 |
| 43 | do | do | 18.57 | 23.50 | 17.80 | − .35 | 16.50 | − .55 | 14.55 | + .85 |
| 44 | do | Soft-mud machine, using mixture of flint and plastic clays | 20.90 | 23.35 | 22.40 | + .45 | 20.50 | + .40 | 19.25 | + .25 |
| 45 | Illinois | Stiff mud | 29.55 | 30.05 | 28.40 | − .65 | 26.70 | −1.75 | 24.10 | − 4.25 |
| 46 | do | do | 22.15 | 22.00 | 20.85 | + .30 | 19.80 | .00 | 18.45 | − .50 |
| 47 | do | do | 24.58 | 25.45 | 21.80 | − .80 | 20.00 | −1.55 | 17.50 | − 2.25 |
| 48 | Ohio | Stiff mud, using mixture of clays | 16.65 | 15.83 | 16.25 | + .55 | 13.75 | + .80 | 11.40 | − .15 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 49 | Pennsylvania | do | 15.35 | 16.70 | 9.15 | + .60 | 9.30 | +3.50 | 8.05 | + 6.50 |
| 50 | do | do | 18.15 | 16.80 | 18.70 | .00 | 18.40 | + .45 | 18.10 | + .35 |
| 51 | do | Handmade, using mixture of clays | 19.44 | 22.75 | 19.75 | + .25 | 19.65 | + .10 | 19.10 | − .15 |
| 52 | West Virginia | Handmade, using mixture of plastic and flint clays | 23.37 | 28.70 | 23.20 | + .65 | 22.20 | + .10 | 19.60 | + .20 |
| 53 | do | Stiff mud, using mixture of plastic and flint clays | 21.15 | 20.05 | 18.80 | + 5.20 | 18.45 | +8.65 | 16.10 | +12.00 |
| 54 | Ohio | Handmade, using mixture of plastic and flint clays | 25.97 | 27.10 | 25.20 | − .65 | 21.55 | −2.30 | 19.50 | − 3.50 |
| 55 | Pennsylvania | do | 22.12 | 22.75 | 21.30 | .00 | 21.00 | − .10 | 19.85 | + .15 |
| 56 | Missouri | Apparently stiff mud | 20.25 | 19.45 | 19.60 | − .35 | 19.25 | − .30 | 17.65 | − .95 |
| 57 | Kentucky | Stiff mud, using mixture of clays | 21.25 | 22.55 | 20.65 | + .35 | 20.50 | .00 | 19.05 | − .35 |
| 58 | Missouri | Apparently stiff mud | 18.69 | 23.40 | 17.75 | − .40 | 16.00 | −1.20 | 14.00 | − 1.55 |
| 59 | do | Dry pressed | 24.58 | 18.28 | 23.80 | + .25 | 24.00 | + .55 | 21.35 | + .55 |
| 60 | Kentucky | Handmade, using mixture of plastic and hard-soft clays | 20.27 | 19.55 | 19.30 | − .05 | 17.10 | − .65 | 15.35 | − .10 |
| 61 | do | do | 20.24 | 21.80 | 16.00 | − 1.15 | 14.25 | −1.50 | 11.60 | − 1.40 |

## TABLE 3.—Results of Tests on Fire Bricks Investigated

[Porosity and volume changes below 1425° C are given in Table 2]

| Laboratory No. of brand | Per cent porosity at 1425° C | Per cent volume change at 1425° C | Per cent porosity at 1450° C | Per cent volume change at 1450° C | Per cent porosity at 1500° C | Per cent volume change at 1500° C | Points decrease in porosity from initial to 1425° C | Points decrease in porosity from initial to 1450° C | Result of load test: deformation in inches and per cent | Softening-point cone |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 9.50 | + 1.75 | 9.00 | + 2.65 | 7.90 | + 4.10 | 4.74 | 5.24 | 0.40 inch=4.48 per cent | 32 |
| 2. | 17.60 | +10.50 | 19.20 | +15.00 | 20.20 | +22.30 | 6.05 | 4.45 | 1.72 inches as temperature reached 1350° C | 20 |
| 3. | 15.75 | + 9.75 | 18.90 | +14.25 | 22.75 | +24.80 | 7.05 | 3.90 | 1.77 inches=20.1 per cent at 1335° C | 20 |
| 4. | 21.40 | .00 | 20.65 | + .90 | 19.60 | + 1.60 | 1.75 | 2.50 | 0.33 inch=3.70 per cent | 33 |
| 5. | 16.75 | + 2.00 | 16.95 | + 2.75 | 15.60 | + 4.40 | 4.53 | 4.33 | Bond gave way after 15 minutes at 1350° C | 31¼ |
| 6. | 16.65 | − 2.80 | 15.75 | − 2.40 | 13.30 | − 1.55 | 7.81 | 8.71 | 1.05 inches=12.1 per cent | 31¼ |
| 7. | 23.00 | +14.40 | 23.40 | +15.50 | ..... | +17.50 | 3.05 | 2.65 | 1.16 inches=13 per cent at 1320° C | 27½ |
| 8. | 19.50 | + 7.75 | 22.95 | +13.75 | ..... | +21.75 | 3.45 | .00 | 1.45 inches=16.5 per cent after 25 minutes at 1350° C | 27½ |
| 9. | 22.50 | .00 | 21.20 | + 1.75 | 19.75 | + 5.40 | 4.32 | 5.62 | Bond gave way at 1345° C | 31¼ |
| 10. | 16.10 | − .75 | 15.00 | + 1.40 | 13.40 | + 4.90 | 13.90 | 15.00 | 1.82 inches=20.1 per cent at 1340° C | 28 |
| 11. | 14.30 | − .25 | 13.25 | − .50 | 11.35 | − .50 | 3.73 | 4.78 | 0.28 inch=3.23 per cent | 29¼ |
| 12. | 12.80 | − 3.40 | 11.80 | − 3.00 | 9.80 | − .95 | 6.70 | 7.70 | 0.49 inch=5.47 per cent | 31 |
| 13. | 12.65 | − 1.60 | 10.00 | − 2.50 | 7.00 | − 3.50 | 1.50 | 4.15 | 0.09 inch=1.06 per cent | 31¾ |
| 14. | 12.30 | − 1.60 | 11.00 | − 1.90 | 7.85 | − 1.75 | 4.03 | 5.33 | 0.44 inch=5.03 per cent | 32 |
| 15. | 14.75 | .00 | 14.65 | + .50 | 14.00 | + 1.10 | 2.08 | 2.18 | 0.27 inch=3.17 per cent | 31¾ |
| 16. | 16.10 | − .25 | 15.40 | .00 | 14.90 | + 1.90 | 5.57 | 6.27 | 0.30 inch=3.5 per cent | 32 |
| 17. | 8.15 | + .75 | 7.60 | + 1.50 | 6.50 | + 4.00 | 4.25 | 4.80 | 0.40 inch=4.6 per cent | 31 |
| 18. | 25.85 | + .40 | 25.85 | + .60 | 24.75 | + .25 | +( .53) | +( .53) | 0.01 inch=0.11 per cent | 29¼ |
| 19. | 25.60 | − .50 | 25.05 | − .90 | 21.60 | − 3.40 | 1.05 | 1.60 | 0.21 inch=2.37 per cent | 31 |
| 20. | 25.60 | − .60 | 25.00 | − .60 | 23.00 | − 2.50 | .00 | .60 | 0.14 inch=1.62 per cent | 32 |
| 21. | 24.30 | − .50 | 23.40 | − .55 | 19.80 | − 2.30 | +( .08) | .82 | 0.28 inch=3.3 per cent | 32 |
| 22. | 22.30 | − 1.25 | 21.35 | − 2.25 | 15.50 | − 5.85 | .77 | 1.72 | 0.23 inch=2.56 per cent | 31 |
| 23. | 17.40 | − .50 | 15.35 | − 1.25 | 10.75 | − 2.00 | 1.68 | 3.73 | 0.10 inch=1.11 per cent | 28 |
| 24. | 17.80 | + .30 | 17.05 | + .15 | 15.00 | − 2 75 | 1 74 | 2.49 | 0.57 inch=6.46 per cent | 31¼ |
| 25. | 18.40 | − .40 | 17.50 | − .50 | 16.50 | − .90 | 1.55 | 2.45 | 0.30 inch=3.45 per cent | 32½ |
| 26. | 6.70 | + 1.20 | 7.50 | + 5.25 | 7.50 | +11.50 | 6.74 | 5.94 | 1.10 inches=12.6 per cent | 29 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 27 | 20 20 | + 5.60 | 19.50 | + 8.00 | 21.25 | +13.15 | 4 35 | 5.05 | 0.79 inch = 9.24 per cent | 32 |
| 28 | 21 00 | — .40 | 21.50 | — .30 | 19 95 | + 3 05 | 6.86 | 6.36 | 1.17 inches after 45 minutes at 1350° C | 31¾ |
| 29 | 12 35 | — 2 50 | 11 40 | — 2 00 | 10 75 | + 1.90 | 8.75 | 9.70 | 0.67 inch = 7.54 per cent | 30 |
| 30 | 20 25 | + 8 00 | 24 60 | +14 80 | 23.90 | +14.65 | .53 | + (3.82) | 2.2 inches at 1315° C | 20 |
| 31 | 18 00 | + .80 | 17 50 | + 1.25 | 15.15 | + 4.55 | 5.63 | 6.13 | Bond gave way after 30 minutes at 1350° C | 29¼ |
| 32 | 18 80 | + 3 10 | 18 30 | + 2 80 | 17.90 | + 5.00 | 4.53 | 5.03 | Bond gave way at 1330° C | 30¾ |
| 33 | 8 25 | — 2 55 | 7 80 | — 1 35 | 13.15 | + 4.30 | 9.70 | 10.15 | 2.25 inches after 30 minutes at 1350° C | 31¼ |
| 34 | 16 40 | — 2.30 | 14.50 | — 0.90 | 14.15 | — 2.05 | 9.58 | 11.48 | Bond gave way at 1345° C. after considerable settle | 28¾ |
| 35 | 14 25 | + 1.00 | 13.70 | — 2.75 | 14.85 | + 5.15 | 7.88 | 8.43 | 1.49 inches after 15 minutes at 1350° C | 28½ |
| 36 | 13 10 | ..... | 10.75 | ..... | 12.90 | ..... | 8.13 | 10.48 | 2.07 inches at 1345° C | 27 |
| 37 | 26 77 | +18 30 | 32.25 | +23.60 | 29.70 | ..... | 3.23 | +(5.48) | 2.07 inches at 1295° C | 26½ |
| 38 | 21 90 | — 5 80 | 20.10 | — 6.30 | 18 00 | — 8.75 | 8.46 | 10.26 | 0.90 inch = 10.4 per cent | 30¼ |
| 39 | 25 30 | — 3 40 | 24.40 | — 3 95 | 22.65 | — 5.45 | 4.80 | 5.70 | 0.89 inch = 10.4 per cent | 30¼ |
| 40 | 14 40 | + 4 65 | 14.50 | + 5 50 | 14 95 | + 8.25 | 9.58 | 9.48 | 1.27 inches after 30 minutes at 1350° C | 31¾ |
| 41 | 18.30 | + .20 | 18 30 | + 1.25 | 18.55 | + 3.60 | 5.77 | 5.77 | 0.75 inch = 8.53 per cent | 33½ |
| 42 | 16 30 | + 1 30 | 16 20 | + 2 50 | 16.00 | + 6.00 | 5.36 | 5.46 | 0.73 inch = 8.31 per cent | 31¾ |
| 43 | 13 70 | + 2.00 | 14 00 | + 3 50 | 13 75 | + 6.85 | 4.87 | 4.57 | Brick bent into S shape after 10 minutes at 1350° C | 29¾ |
| 44 | 18 90 | + .20 | 19 00 | + 1 00 | 18.60 | + 1.65 | 2.00 | 1.90 | 0.42 inch = 4.78 per cent | 33¼ |
| 45 | 22 55 | — 5 70 | 21 00 | — 7 00 | 16 90 | — 9 40 | 7.00 | 8.55 | 0.48 inch = 5.33 per cent | 31 |
| 46 | 17 65 | — .80 | 17 10 | — 1 00 | 14 15 | 2 90 | 4.50 | 5.05 | 0.40 inch = 4.47 per cent | 29 |
| 47 | 16 20 | — 2 50 | 15 50 | — 3 40 | 12 60 | — 5 05 | 8.38 | 9.08 | 0.78 inch = 8.76 per cent | 30 |
| 48 | 10 50 | — .60 | 10 30 | .00 | 9 50 | + 3 75 | 6.15 | 6.35 | 0.41 inch = 4.67 per cent | 31¼ |
| 49 | 7 35 | + 8 00 | 7 75 | +10 10 | 8.70 | +15 00 | 8.00 | 7.60 | 0.83 inch = 9.37 per cent | 31¾ |
| 50 | 17 90 | + .25 | 17 75 | + .25 | 17 00 | + .70 | .25 | .40 | 0.23 inch = 2.6 per cent | 32½ |
| 51 | 18 60 | — .50 | 17 76 | — 1 00 | 15 35 | — 5 10 | .84 | 1.68 | 0.82 inch = 9.3 per cent | 32 |
| 52 | 18 30 | + .30 | 18 50 | + 1 00 | 17.25 | + 2.35 | 5.07 | 4.87 | 0.78 inch = 8.9 per cent | 32 |
| 53 | 14 85 | +13 60 | 15 00 | +15 85 | 15 50 | +20.70 | 6 30 | 6.15 | 2.05 inches at 1335° C. bond gave way | 29¼ |
| 54 | 19 00 | — 3 80 | 18 60 | — 4.00 | 17.25 | — 4.20 | 6 97 | 7.37 | 0.45 inch = 5.09 per cent | 32 |
| 55 | 19 10 | + .40 | 18 20 | + .75 | 16 10 | + 1.25 | 3.02 | 3 92 | 0.50 inch = 5.63 per cent | 31¼ |
| 56 | 16 60 | — 1 50 | 16 10 | — 2 25 | 13 30 | — 4 10 | 3 65 | 4 15 | 0.18 inch = 2.06 per cent | 32¼ |
| 57 | 18 00 | — .55 | 16 75 | — .80 | 14 35 | — 2 15 | 3 25 | 4 50 | 0.16 inch = 1.77 per cent | 32¼ |
| 58 | 13 00 | — 1 50 | 11 75 | .75 | 10 05 | — 1 00 | 5.69 | 6.94 | 0.42 inch = 4.7 per cent | 29¼ |
| 59 | 19 20 | + .60 | 16 75 | + .60 | 14.20 | + 3 10 | 5 28 | 7 83 | 0.52 inch = 5.8 per cent | 29 |
| 60 | 14 75 | + .40 | 14 50 | + 1 00 | 14 10 | + 6.60 | 5.52 | 5.77 | 0.31 inch = 3.5 per cent | 31¼ |
| 61 | 10 50 | — 1 15 | 11 00 | — .50 | 10 50 | + 1 35 | 9 74 | 9.24 | 0.72 inch = 7.98 per cent | 31 |

It is well to add before discussing the results in Tables 2 and 3 that most of the bricks tested were of a nonsiliceous character, as inferred from the information furnished by the manufacturer and from other considerations. However, some of the bricks were apparently of a siliceous nature, or their character in this respect was doubtful. Therefore, a chemical analysis was made on these few bricks to determine the silica, alumina, and iron oxide. The results are given in Table 4. It is to be regretted that, owing to the time and expense involved, it was not possible to make a complete chemical analysis of all the bricks studied in this investigation. A knowledge of the chemical analysis is always desirable in making a study of the fundamental properties of fire bricks.

TABLE 4.—Partial Chemical Analyses of Some of the Fire Bricks Investigated

| Laboratory No. of brand | $SiO_2$ | $Al_2O_3$+ $TiO_2$ | $Fe_2O_3$ | CaO+ MgO+ $Na_2O$+ $K_2O$ | Total fluxes excluding $TiO_2$, but including iron as FeO |
|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent by difference | Per cent |
| 11 | 65.93 | 31.31 | 2.96 | 0.00 | 1.33 |
| 18 | 80.56 | 18.69 | 1.15 | .00 | .52 |
| 19 | 69.92 | 28.45 | 2.00 | .00 | .90 |
| 22 | 67.47 | 30.38 | 1.48 | .67 | 1.33 |
| 23 | 75.66 | 21.69 | 2.22 | .43 | 1.43 |
| 24 | 60.07 | 34.88 | 2.22 | 2.83 | 3.83 |
| 46 | 73.37 | 24.55 | 2.39 | .00 | 1.07 |

## V. DISCUSSION OF RESULTS

A study of the data presented in Tables 2 and 3 shows some interesting relationships between the porosity and volume changes and the results of the load tests. In nearly all cases of bricks which successfully withstood the load test, showing a deformation of not more than 5.55 per cent, there is comparatively little volume change by either expansion or contraction up to 1425° C, while a considerable number of the bricks which failed in the load test show very appreciable volume changes. Similarly, the porosity decrease in the case of bricks which pass the load test is not large, while many of those which failed show considerable decrease in porosity at some point below 1425° C. In many cases overburning of bricks of poorer grade is distinctly evident from the volume and porosity changes. The sudden and more or

less pronounced expansion at the lower temperatures of firing in the case of some of the bricks (2, 3, 7, 8, etc.) is certain evidence of overburning which is confirmed by the results in the load test. An abrupt increase in porosity at the same or at a slightly higher temperature is usually noted in such cases. Invariably such bricks failed in the load test. Bricks which show either marked volume change or a considerable decrease in porosity also failed to withstand the load test.

It would seem, then, that the volume and porosity changes of clay fire bricks might serve in some measure as a criterion of their ability to withstand load at high temperatures. A careful study of the data for various burning temperatures shows some pertinent points in this connection, and the specimens will be considered in the order of the reheating temperatures.

1350°C.—Of 26 bricks which passed in the load test 23 show not more than 1 per cent volume change; 3 show more than 1 per cent. Of 35 bricks failing in the load test (showing more than 5.55 per cent deformation), 16 show not more than 1 per cent volume change and 19 more than 1 per cent.

Of 26 bricks passing the load test 25 show not more than 3 per cent porosity decrease; 1 more than 3 per cent. Of 35 failing in the load test, 13 show not over 3 per cent and 22 more than 3 per cent porosity decrease.

Combining these criteria, 33 of 61 show not more than 1 per cent volume change nor more than 3 per cent porosity decrease, 23 of these passing and 10 failing the load test. Of those showing more than 1 per cent volume change or more than 3 per cent decrease in porosity, 3 passed and 25 failed the load test.

1400°C—.Not over 2 per cent volume change was shown by 23 bricks which passed and 15 which failed in the load test. Of 23 bricks which showed over 2 per cent volume change, 3 passed and 20 failed in the load test.

Of 36 bricks showing not over 5 per cent decrease in porosity, 22 passed and 14 failed in the load test. Of 25 showing more than 5 per cent porosity decrease, 3 passed and 22 failed in the load test.

Of the bricks which showed neither a volume change greater than 2 per cent nor a porosity decrease exceeding 5 per cent, 22 passed and 10 failed in the load test.

On the basis of a volume change not exceeding 3 per cent at 1400° (amounting to about 1 per cent linear expansion or contraction), 24 passed and 19 failed in the load test. Of those exceeding 3 per cent volume change, 2 passed and 16 failed in the load test.

Excluding bricks which showed more than 3 per cent volume change or 5 per cent porosity decrease, 22 passed and 10 failed in in the load test. Of those which showed either more than 3 per cent volume change or 5 per cent porosity decrease, 4 passed and 25 failed in the load test.

1425°C.—Of 38 bricks showing not more than 2 per cent volume change, 23 passed and 15 failed the load test. Of those showing more than 2 per cent volume change, 3 passed and 20 failed the load test.

Of 34 bricks showing not over 5 per cent porosity change, 21 passed and 13 failed the load test. Of those showing more than 5 per cent porosity decrease, 6 passed and 21 failed in the load test.

Of the bricks which neither changed more than 2 per cent in volume nor 5 per cent in porosity, 20 passed and 7 failed in the load test. Of those changing more than 2 per cent in volume or 5 per cent in porosity, 6 passed and 28 failed in the load test.

It is apparent that the porosity and volume changes of clay fire bricks when burnt at some temperature between 1350 and 1425°C, offer, in some degree, a criterion of their ability to withstand the load test. The bricks passed or rejected by the suggested limitations in porosity or volume changes at the various temperatures are nearly the same in all cases. This consistency indicates that the apparent relation between these changes and the ability of bricks to withstand the load test is more than a chance one and that certain limitations in this respect might well be used as a means of rejection of a large number of bricks which would undoubtedly fail in that test. The use of either porosity or volume changes alone offers a fairly satisfactory criterion. Taken together the result is even better, since a number of bricks failing in the load test can pass one or the other specifications as regards volume or porosity change, but few of the better bricks fail to pass both.

For practical purposes a temperature should be selected which is not too high to be readily attained under ordinary conditions, but high enough so that the limitations in porosity or volume changes need not be too close to be easily measured. Probably 1400 or 1425° C would be the best temperature. From the results here obtained a temperature of 1400°C would seem most satisfactory, since the permissible limit in volume change may be made as high as 3 per cent, this practically amounting to a linear

contraction or expansion of 1 per cent. A limit of 5 per cent in porosity decrease is quite satisfactory. At this temperature also the effects of overburning in the inferior materials is likely to become sufficiently evident to be readily detected. Nearly all of the bricks which successfully withstand the load test could meet these specifications, while a majority of those that fail under load would be eliminated by excessive volume or porosity change, or both. It may be noted that in all cases bricks which showed a porosity decrease exceeding 5 per cent or a volume change exceeding 3 per cent showed a deformation in excess of 5 per cent in the load test, close to the permissible limit.

In the case of clay fire bricks an increase in volume is especially significant, as it represents evidence showing that overfiring has taken place due to a comparatively high content of fluxes. It is important, therefore, that the permissible expansion be rigidly limited to a definite value, which must be lower than that for the allowable contraction.

In the case of some of the bricks failing in the load test due to failure of the bond there were no marked changes in either volume or porosity. Generally such bricks have a very low cold crushing strength, as in the case of No. 5, which failed under a load of 365 pounds per square inch, and No. 9, which crushed at 385 pounds per square inch. The minimum allowable cold crushing strength for a No. 1 refractory is generally placed at 1000 pounds per square inch.

There is apparently little relation between the softening points and the volume and porosity changes or with the results of the load test. Some of the bricks showing high softening temperatures failed to withstand this test, while several which softened below cone 31 showed less than 5 per cent deformation. The latter were probably siliceous in character, containing more than 65 per cent $SiO_2$. In some cases where bricks failed the high softening point is probably due to the intimate mixture of the inferior bonding clay with the more refractory flint clay in the preparation of the test cones, the material being ground to 60-mesh size. In all cases bricks showing softening points lower than cone 28 failed completely in the load test. It may be considered, then, that cone 28 should be the minimum softening temperature of a No. 1 refractory of either siliceous or nonsiliceous character.

In Fig. 2 are shown porosity and volume change curves for six bricks of different characteristics which successfully withstood the load test. These have been selected as fairly typical of the bricks of this class. Contraction is indicated by negative volume change, expansion by positive values.

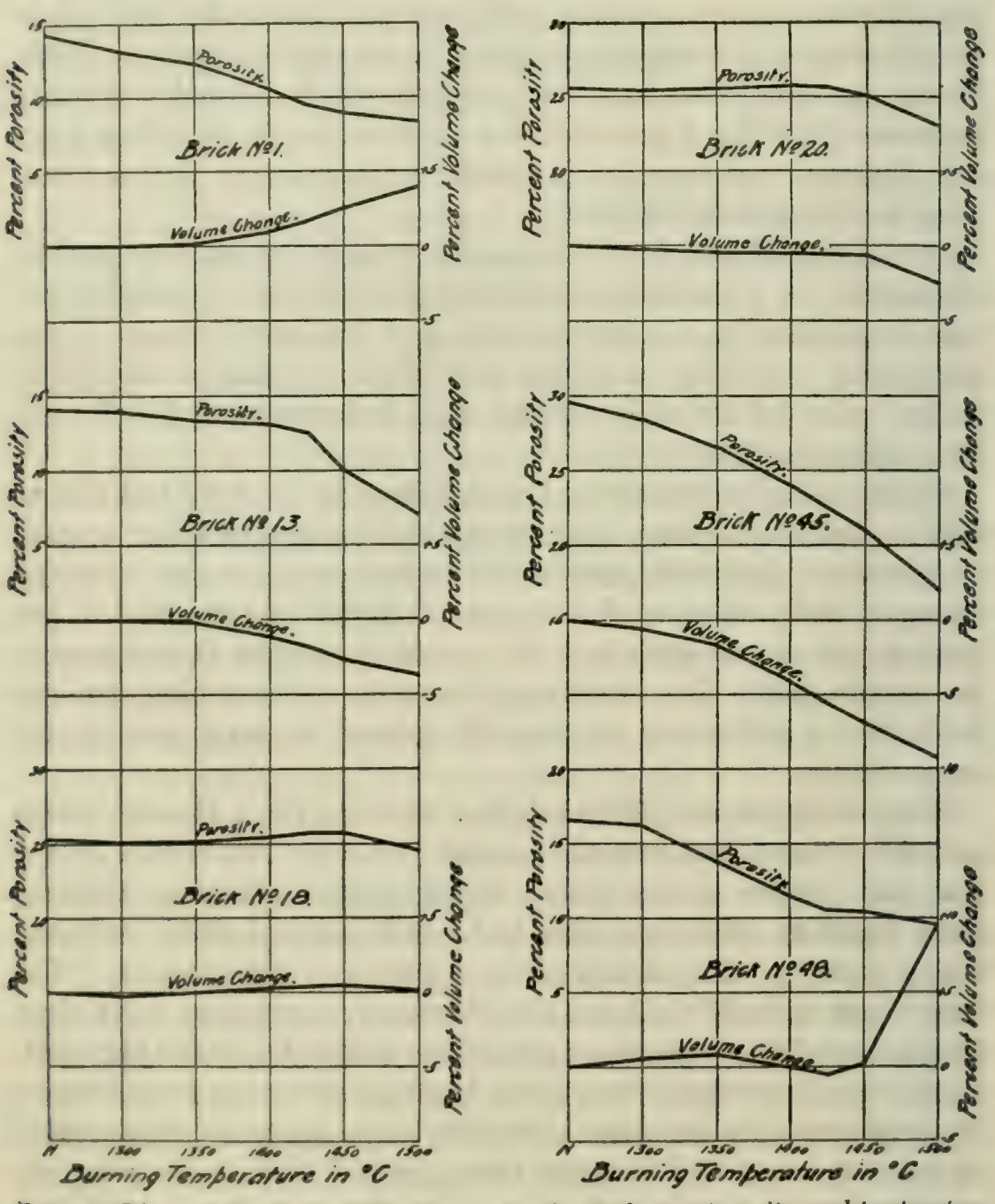


FIG. 2.—*Diagram showing relation between volume change, porosity, and temperature*

In the curves for brick No. 1 a gradual expansion, accompanied by a gradual decrease in porosity, is noted. The low initial porosity is characteristic of the stiff-mud brick. The gradual expansion would seem to indicate a siliceous character; but this seems unlikely in view of the high softening point, cone 32. The result of the load test was a deformation of 4.47 per cent.

Brick No. 13 shows gradual contraction beyond 1350° C, accompanied by an increased rate of porosity decrease above 1425° C. This is also a stiff-mud brick with low initial porosity and a softening point of cone 31¾. The deformation in the load test was slight, only 1.06 per cent.

Brick No. 18, made by dry pressing, is apparently siliceous in character, as indicated by the slight expansion on heating and the very slight porosity changes. The slight deformation in the load test, 0.11 per cent, and the softening temperature at cone 29¼, which is too low for a nonsiliceous material of this quality, also indicate a high silica content. The chemical analysis shows 80.56 per cent $SiO_2$ and a very low content of fluxes.

Brick No. 20, handmade from a mixture of flint and plastic clays, represents a high clay brick of excellent refractoriness. The porosity curve shows the characteristics of flint clays in the slight changes up to 1425° C. No appreciable volume of change occurs below 1450° C. The softening point is at cone 32, and the deformation in the load test was only 1.62 per cent.

Brick No. 45 showed a deformation of 5.33 per cent in the load test, close to the allowable limit. The large amounts of contraction and porosity decrease would render the quality of this brick doubtful in the light of the suggested specifications in this respect. The regularity of the porosity decrease and contraction indicates a gradual and continuous fluxing action, but with no indication of overburning. The softening point of this material was cone 31.

Brick No. 48 shows a rapid porosity decrease above 1300° C. The volume change is slight, up to 1425°, where overburning is indicated by the subsequent expansion. While the deformation in the load test (4.47 per cent) fell within the limit, the porosity change exceeds 5 per cent. The ability of this brick to withstand long-continued heat treatment at high temperatures would be somewhat doubtful, due to its overburning tendencies. The softening point was at cone 31¼.

In Fig. 3 are shown curves for some of the bricks which failed to pass the load test. Brick No. 26, with a deformation of 12.6 per cent, shows a gradual expansion above 1300° C, becoming rapid above 1400°. The increase in porosity at 1425° indicates that this is probably due to the gradual development of vesicular structure by overburning.

Brick No. 38 shows marked but gradual fluxing in its rapid decrease both in porosity and volume. It is evidently not of a siliceous character and of only fair refractoriness. The softening

point at cone 30¼ and the deformation in the load test (10.4 per cent) confirm this.

Brick No. 41 begins to overburn at 1300°, as indicated by the expansion and by the break in the porosity curve at a somewhat higher temperature. The high softening point, cone 33½, is

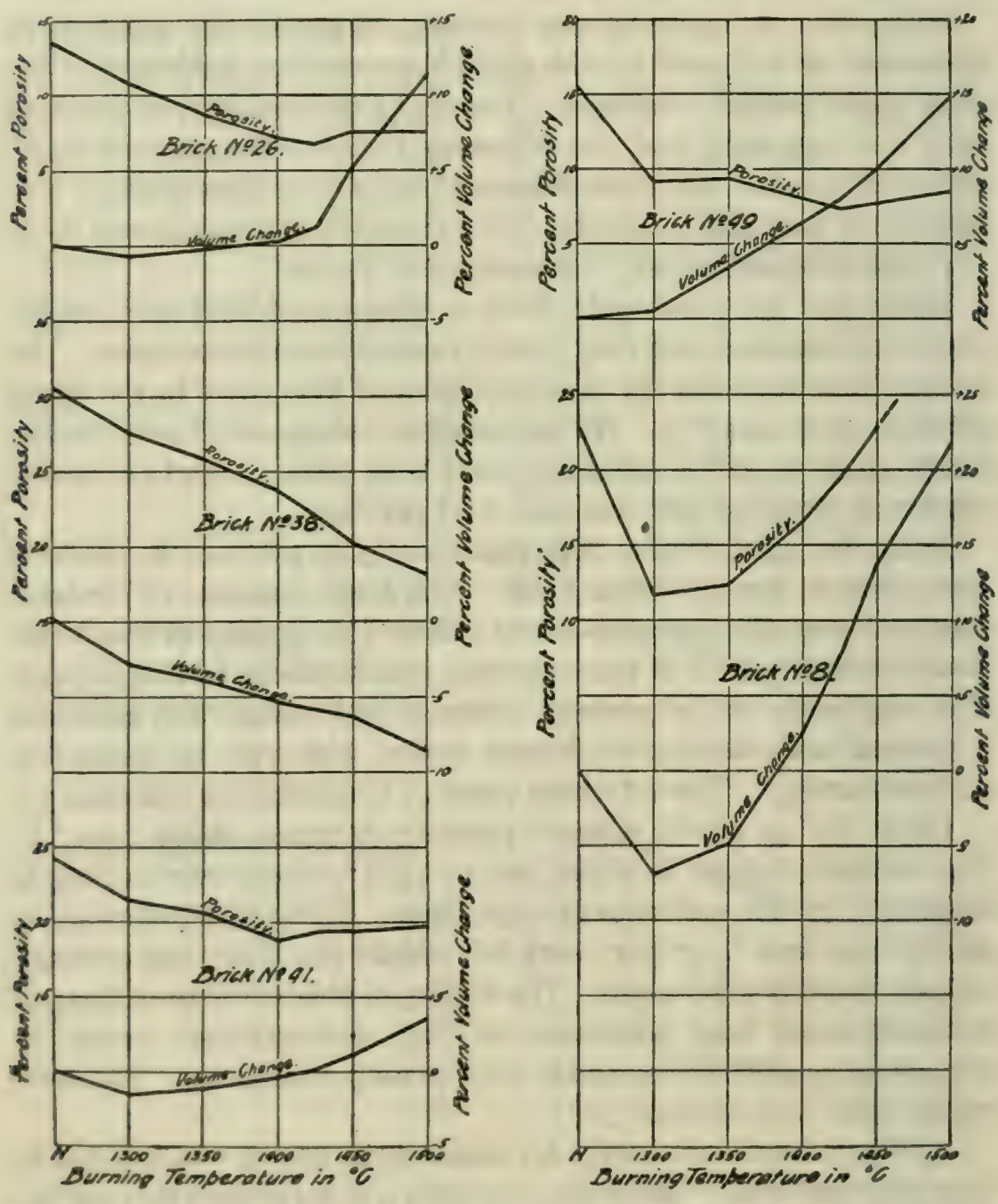


FIG. 3.—*Diagram showing relation between volume change, porosity, and temperature*

apparently the result of the fine grinding of the material in preparing the test cones. The failure to pass the load test is probably due to an inferior bond clay in the mixture.

Brick No. 49, also made from a mixture of clays, shows overburning by expansion above 1300° and the break in the porosity

curve. The softening point is at cone 31¼, and the deformation in the load test was 9.37 per cent.

Brick No. 8 is typical of a number of those which failed completely in the load test. It has a low softening point, cone 27½, and shows marked overburning above 1300° C by the rapid expansion and by the increase in porosity. The decided contraction and decrease in porosity when burnt at 1300° C indicate a low temperature of burning in manufacture.

It was also found that the average brick with an initial porosity below 21.50 per cent and which did not show evidence of overfiring to the extent referred to above had a contraction in the load test of one-half inch in a length of 9 inches, with an average decrease in percentage of porosity, up to 1425° C, of about six points. On the other hand, the average brick with an initial porosity above 21.50 per cent showed a like contraction in the load test with a change in percentage of porosity of about three points.

## VI. PRACTICAL APPLICATION OF POROSITY AND VOLUME MEASUREMENTS OF CLAY FIRE BRICKS

The determination of porosity or volume changes of clay fire bricks, burnt at some temperature between 1350 and 1425° C, affords a means of separating a certain proportion of bricks which would fail in the load test. The limits of 3 per cent in volume change (or 1 per cent in linear contraction or expansion) and 5 per cent decrease in porosity at 1400° C do not eliminate all bricks which can not withstand such a test, but materially reduce the number which would require such testing. In this respect it would be of considerable advantage in comparing the quality of a large number of samples, since the porosity and volume changes may be determined readily from a single burn in a test kiln. To make standard load tests on a number of bricks requires considerable time and expense, even if several furnaces were available.

The determination of volume changes is comparatively simple when porosities are also determined, since the difference in the wet and suspended weights of the specimens affords a measurement of volume practically as accurate as by means of the volumenometer.

The porosity and volume changes in burning may also be used advantageously as a means of determining the uniformity of quality of a lot of bricks of a single brand. The behavior of such bricks should be fairly uniform if they be of equal quality. Such

application of these measurements would be of value to the manufacturer, as well as to the consumer.

A study of the curves for porosity and volume changes for a series of burning temperatures offers a means of determining, in some measure, the causes of failure of certain bricks in the load test. If this be due to underburning, resulting in excessive deformation under load due to shrinkage, a considerable decrease in porosity and volume will be found at the lower burning temperatures. Clays of inferior quality which overburn will be detected by marked expansion at some point in the burning, usually accompanied at a somewhat higher temperature by an increase in porosity due to vesicular structure. Clays lower in fluxes, and which do not readily develop vesicular structures, show gradual but marked contraction and decrease in porosity as the burning temperature is increased.

## VII. SUMMARY

1. Bricks which are capable of withstanding a pressure of 40 pounds per square inch at 1350° C generally show slight changes in volume or porosity when burnt at temperatures up to 1425° C.

2. The greater number of the bricks which failed to pass the load test show rather marked change in volume or in porosity at some temperatures below 1425° C.

3. Bricks which show distinct overburning by pronounced expansion at temperatures below 1400° C invariably fail in the load test. The adoption of a definite limit for the permissible expansion within the given temperature range is particularly important for detecting inferior clay refractories. The limit of expansion should be lower than that for the allowable contraction.

4. The changes in volume and in porosity of bricks burnt at some temperature between 1350° C and 1425° C serves, in a measure, as a criterion of their ability to pass the load test.

5. Most of the bricks which show a porosity decrease not exceeding 5 per cent and a volume change not exceeding 3 per cent (approximately 1 per cent in linear dimensions), when burnt at 1400° C, will pass the load test.

6. Bricks which show a decrease in porosity exceeding 5 per cent, or an expansion or contraction in excess of 3 per cent by volume (1 per cent in length) at 1400° C, in nearly all cases failed to pass the load test.

7. The use of limiting porosity and volume changes for clay fire bricks burnt at 1400° C would serve as a means of eliminating

from consideration a large number of bricks which fail in the load test.

8. Bricks which fail in the load test due to failure in the bond may not show marked changes in volume or porosity in burning, but often show very low cold crushing strength.

9. No definite relationship seems to exist between the softening point of a fire brick and its ability to withstand load at high temperatures. However, all bricks which softened below cone 28, whether siliceous or not in character, failed completely in the load test. It seems advisable, then, to specify cone 28 as the minimum softening point for any clay fire brick. It is probable that bricks containing less than 65 per cent $SiO_2$ should have a minimum softening point of cone 31.

10. Bricks with an initial porosity below 21,5 per cent and with an average decrease of about six points in percentage of porosity contracted about 5.5 per cent in the load test. Bricks showing an average porosity above 21.5 per cent showed a like contraction in the load test with a change of about three points in porosity percentage.

In conclusion, the writer desires to express his appreciation of the assistance rendered by D. W. Ross, in conducting the load tests of this investigation, and to thank A. V. Bleininger for valuable suggestions in carrying out the work.

WASHINGTON, October 12, 1919.

DEPARTMENT OF COMMERCE

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## No. 160

## EFFECTS OF OILS, GREASES, AND DEGREE OF TANNAGE ON THE PHYSICAL PROPERTIES OF RUSSET HARNESS LEATHER


BY

R. C. BOWKER, Assistant Mechanical Engineer

*Bureau of Standards*

in cooperation with

J. B. CHURCHILL, Director

*American Leather Research Laboratory*



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By R. C. Bowker and J. B. Churchill

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Methods | 4 |
| 1. Selection of the leather | 4 |
| (*a*) Description of the leather selected | 4 |
| (*b*) Preparation of samples | 6 |
| 2. Physical tests | 7 |
| (*a*) Tensile strength | 7 |
| (*b*) Stretch | 7 |
| (*c*) Buckle strength | 8 |
| 3. Chemical tests | 8 |
| (*a*) Stuffing content | 8 |
| (*b*) Complete analysis | 8 |
| III. Data and results obtained | 9 |
| 1. Physical tests | 9 |
| (*a*) Tensile strength | 9 |
| (*b*) Stretch | 12 |
| (*c*) Buckle strength | 13 |
| 2. Chemical tests | 14 |
| (*a*) Stuffing content | 14 |
| (*b*) Complete analysis | 15 |
| 3. Comparison of physical and chemical tests | 16 |
| (*a*) Effect of the amount of stuffing content on the physical properties | 16 |
| (*b*) Effect of the degree of tannage on the physical properties | 17 |
| (*c*) Effect of animal and mineral oils on the physical properties | 18 |
| IV. Conclusions | 18 |


## I. INTRODUCTION

During the war physical and chemical tests of the equipment leather purchased by the War Department were made at the Bureau for the purpose of controlling the quality of the leather furnished by the various tanneries. An opportunity was thus offered for a study of the variations in the physical properties and in the chemical constituents of many kinds of leather. On account of the large quantities used the values of the various

properties for both russet and black harness leathers were of special interest. Russet harness leather is not a regular commercial product in this country and finds little use except for military purposes. Black harness leather, however, is a regular commercial product and is widely used. Besides the difference in color, there are three distinct differences between these two leathers caused by the process of manufacture. The first of these differences occurs in the length of the tanning operation. It is general practice to give hides for black harness leather a short-time tannage, while those for russet harness leather are tanned for a longer time. The average degree of tannage as determined from the chemical analyses of black and russet harness leathers made during the war were 46 and 61, respectively. The second point of difference between these two kinds of leather is shown by the amount of stuffing used. The average amounts found in the above-mentioned black and russet leathers were 29.3 and 15.5, respectively. The third difference is caused by the general practice of adding to black harness leather small amounts of such filling materials as glucose and salts. This procedure is not generally followed in the case of russet harness leather. A better selection of hides is generally used for the latter leather, since the coloring of black harness readily conceals many surface imperfections which do not affect the quality. In order to study more definitely the effects of the amount and kind of stuffing content and also the degree of tannage on the physical properties of harness leather, this investigation was made.

## II. METHODS

### 1. SELECTION OF THE LEATHER

Russet harness leather was used in this investigation. Three hides were prepared, marked butt Nos. 1, 2, and 3, to study the effects of different amounts of stuffing content, of animal and mineral oils, and of medium and heavy tannage, respectively, on the physical properties.

The method of using whole hides or double backs in preparing this leather was used, so that, when split, each single back could be given its special finishing treatment and when tests were made the leather of the two sides compared would come from the same hide. Each side was given a code letter.

(*a*) DESCRIPTION OF THE LEATHER SELECTED.—The hides from which the leather was produced were treated in the usual manner,

which consisted of soaking, fleshing, liming, unhairing, handling, and then laying away in the yard. The tanning materials used were liquors made from chestnut-oak bark, chestnut wood, and quebracho. After the tanning was completed the hides were split, shaved, scoured, and bleached with a solution of soda and water, sulphuric acid and water, and sumac and water. The leather was then stuffed and later oiled. The finishing was done by hand.

*Butt No. 1.*—This hide received the regular tannage for this type of leather and, after being split, one side (*B*) was stuffed with a mixture of cod oil and tallow, using the amount ordinarily used in the particular tannery where the leather was made. The other

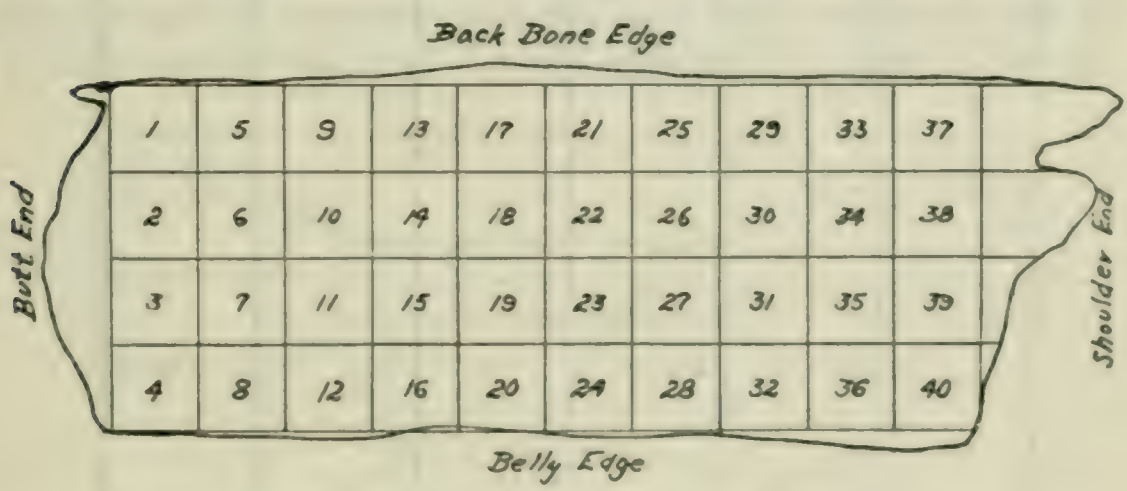


FIG. 1.—*Division of a side into blocks*

side (*A*) was stuffed with a larger amount of the mixture, equal approximately to that used by some tanners of black harness leather. These two sides were used to study the effects of different amounts of stuffing content on the physical properties.

*Butt No. 2.*—The leather produced by this hide was used to study the effects of a medium and heavy tannage on the physical properties. The hide, after receiving the regular tanning treatment, was split and one side (*C*) removed, while the other side (*D*) was allowed to remain in the vats a month longer in order to receive a heavier tannage.

*Butt No. 3.*—This hide, after being tanned as regular russet harness leather, was split and one side (*E*) was stuffed with a mixture of 50 per cent cod oil and 50 per cent tallow. The other side (*F*) was stuffed with a mixture of 50 per cent Breton mineral oil and 50 per cent tallow. This leather was prepared to determine, if possible, the effects of the use of mineral and animal oils on the physical properties of leather.

(*b*) PREPARATION OF SAMPLES.—Each side of leather was divided into 40 blocks, as shown in Fig. 1, beginning at the butt end, near the root of the tail, with block No. 1 and running across the hide from back to belly. The blocks running from the butt end to the shoulder end were numbered in steps of four. The size of each block was approximately 8 inches in length and 7 inches in width. Each was divided into samples for the various tests, as

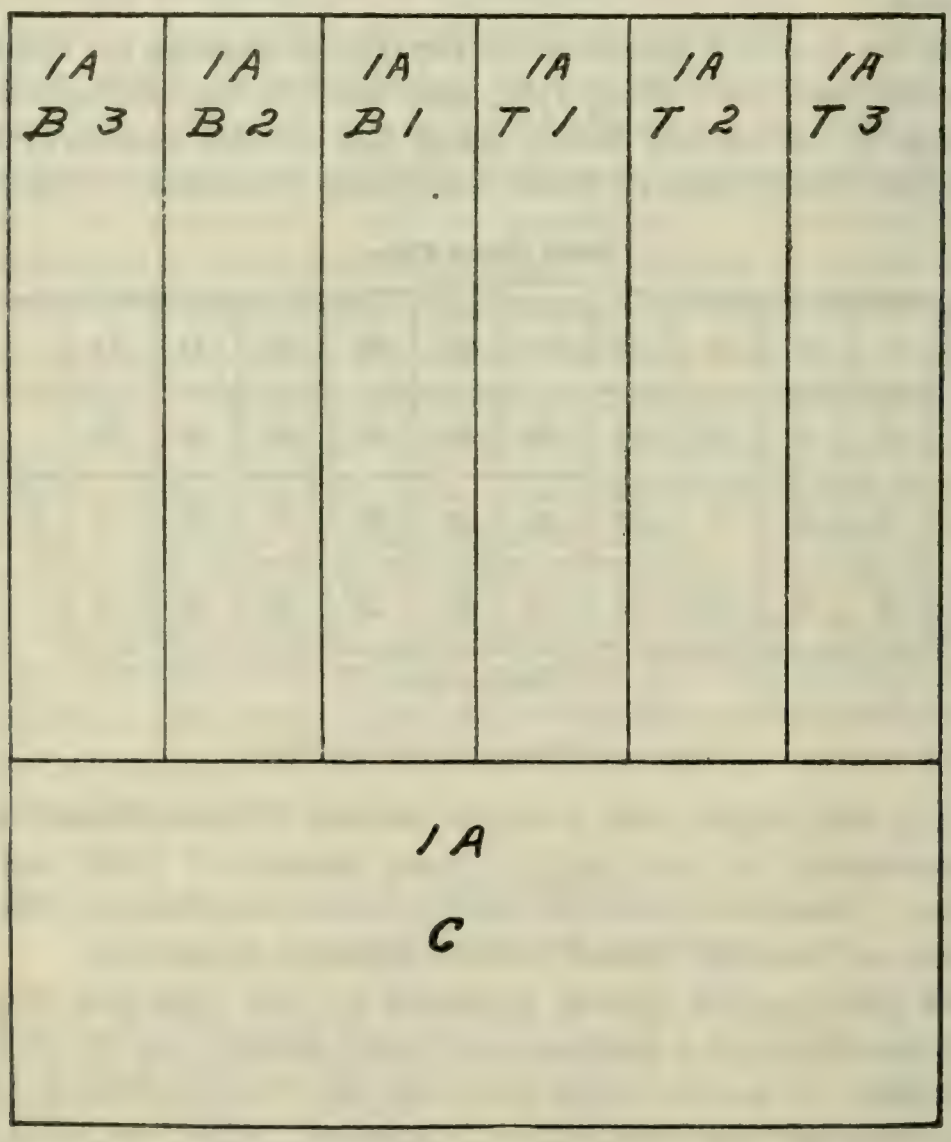


FIG. 2.—*Division of a block into samples for the different tests*

shown in Fig. 2. Three samples from each block, designated by *T1*, *T2*, and *T3*, were prepared for the tensile strength and elongation tests, and three samples, designated by *B1*, *B2*, and *B3*, were used for the buckle tests. That part of each block used for the chemical tests is designated by the letter *C*. Each sample cut from any block carried the code letter of the bend, the number of the block, and the letter representing the test for which the sample was to be used.

## 2. PHYSICAL TESTS

The physical tests generally made on samples of harness leather for determining the quality are for tensile strength and percentage elongation. In addition, a buckle or shearing test was made.

(*a*) TENSILE STRENGTH.—This is the test most commonly made, the results being expressed in pounds per square inch. Test pieces were cut with a metal die from each individual strip. The shape and size of the resulting sample are shown in Fig. 3. The ends are enlarged and the central portion is reduced to a width of one-half inch over a gage length of 2 inches. This shape usually insures that the sample will break within the reduced section and prevents tearing in the grips of the testing machine. The breaking strength, in pounds, of each sample was determined with a tension machine the jaws of which separated at a rate of approx-

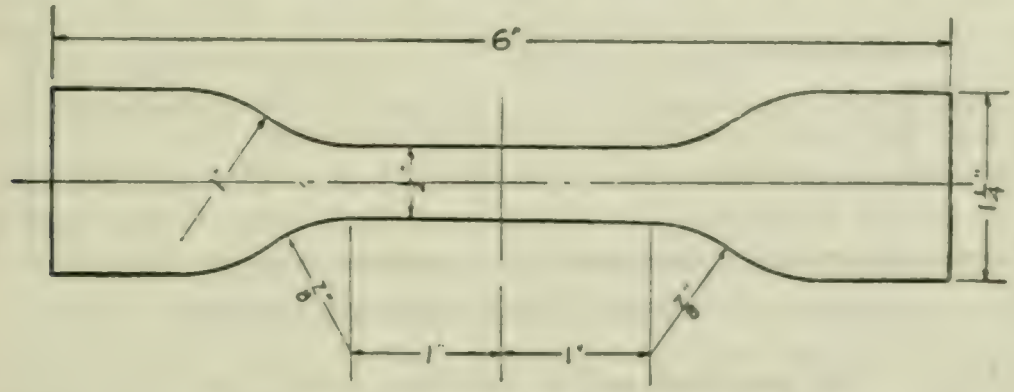


FIG. 3.—*Shape and size of tensile strength specimens*

imately 6 inches per minute. With this value and the area, as determined by the width and thickness of the reduced section, the tensile strength in pounds per square inch was calculated.

The breaking strength, in pounds per inch of width, was also determined. There were three values for each of these properties for each block and an average of the three for each property was used as representing the value for the particular location on the side indicated by the block number.

(*b*) STRETCH.—The stretch, or percentage elongation, of each tension test piece was determined at the breaking strength. The method consisted of first marking on the reduced section parallel lines 2 inches apart. A convenient method of noting the stretch, used in this test, consisted of following the parallel lines on the test pieces, as they separated under the tension, with a pair of dividers. The elongation was then measured with a scale and the percentage increase calculated. In this case also the average of three values represented the value for the block.

(*c*) BUCKLE STRENGTH.—There are many parts of a harness which are used in conjunction with a buckle. It is common knowledge that the failure of a particular strap or part of a harness often occurs at one of the holes through which the tongue of the buckle passes. It was thought desirable to study the variation on the hide in the buckle or shearing strength of new harness leather with the idea in view of showing what portions of the hide might be most suitable for those straps which are used with a buckle. Three samples for this test were prepared from each block, as shown in Fig. 4. A hole of the proper size for the buckle tongue was punched 1 inch from the end of the test piece. An ordinary 1¼-inch harness buckle with a tongue approximately .eighteen-hundredths of an inch in diameter was secured to a strap which was placed in one jaw of the testing

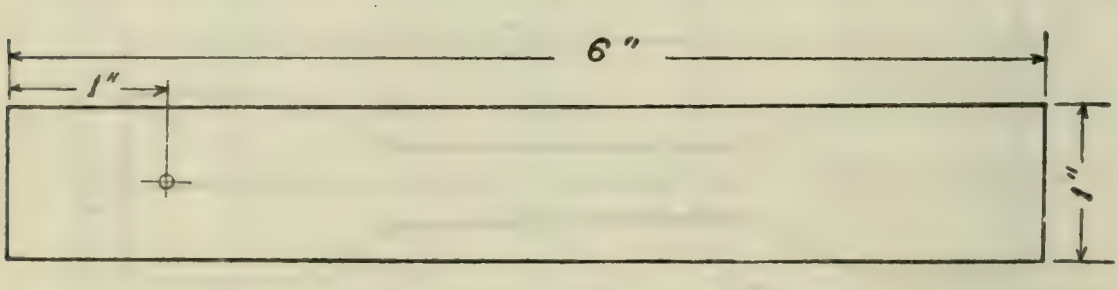


FIG. 4.—*Shape and size of buckle strength specimens*

machine. The punched end of the test piece was then inserted in the buckle and the free end secured in the other jaw of the machine. The number of pounds required to pull the test piece through the buckle was then noted.

### 3. CHEMICAL TESTS

(*a*) STUFFING CONTENT.—It was considered possible that the variation in the amount of stuffing content over the hide might have some effect on the physical properties. For this reason, and also to study the distribution of the stuffing content over the hide, a chemical determination was made of this property for each block of each side.

(*b*) COMPLETE ANALYSIS.—In order to aid in the interpretation of the physical results, and also to have all the data possible for the identification of the several sides, a complete chemical analysis was made of each, using a composite sample prepared by taking an equal quantity from each block.

## III. DATA AND RESULTS OBTAINED

### 1. PHYSICAL TESTS

(*a*) TENSILE STRENGTH.—The results of the tensile-strength tests, expressed in pounds per square inch, are shown graphically in Figs. 5, 6, and 7. Each individual curve of the graphs represents

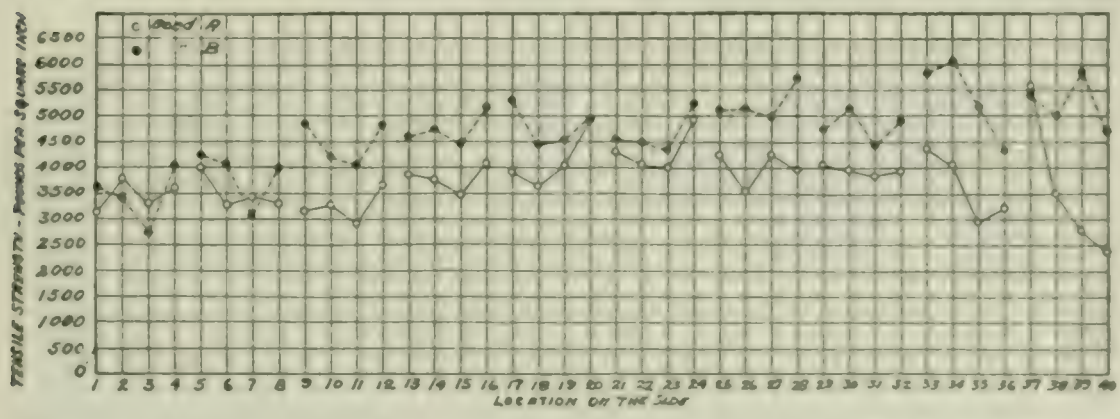


FIG. 5.—*Variation of tensile strength in pounds per square inch over the side for samples A and B*

the values obtained from four blocks running from the backbone edge to the belly edge. The values for the tensile strength, in pounds per inch of width, are shown graphically in Figs. 8, 9, and 10. For that portion of any side represented by blocks 1 to 28, inclusive, the strength is generally greater on the backbone edge, decreasing in value toward a point near the belly edge, beyond

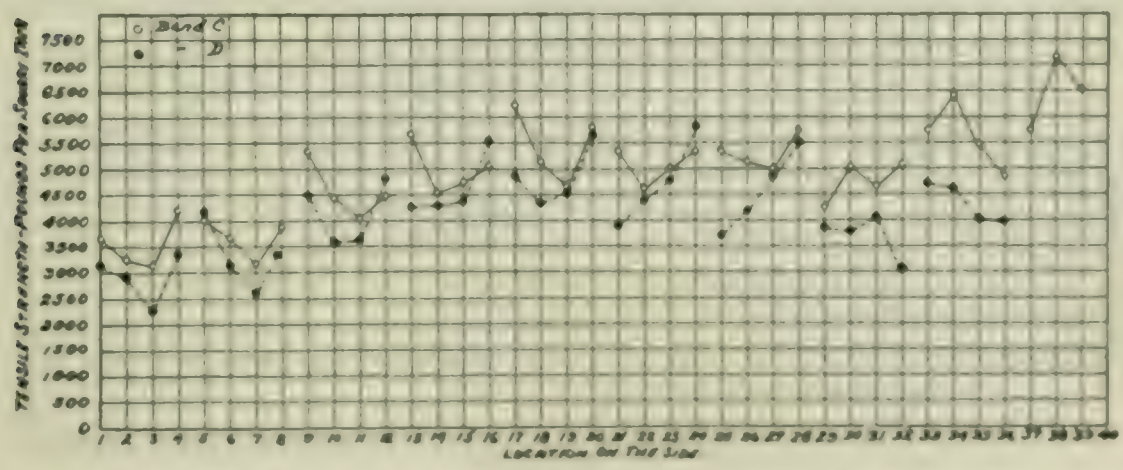


FIG. 6.—*Variation of tensile strength in pounds per square inch over the side for samples C and D*

which it generally increases to either an equal or greater value than occurred on the backbone. That portion of the sides represented by blocks 29 to 40, inclusive, is the shoulder area. The strength in that part is more irregular than in the other portion, but has a general tendency to be greater at the backbone edge

and to decrease steadily to the belly edge. A glance at Figs 8, 9, and 10 will show that the average tensile strength, in pounds per inch of width, for any given section of four blocks across a side is generally low at the butt end, increasing in value up to locations 17 to 20, or about half the length of the side, then decreasing in value, ending with the first shoulder section 29 to 32,

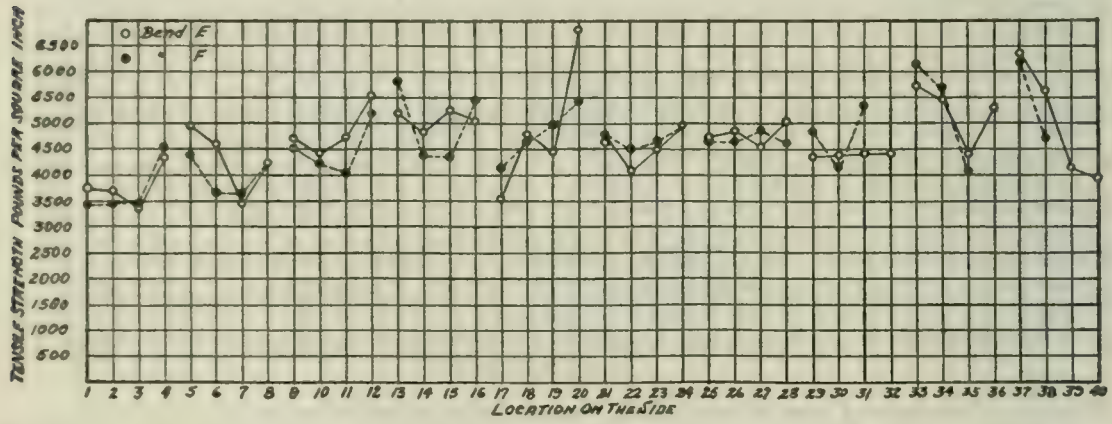


FIG. 7.—*Variation of tensile strength in pounds per square inch over the side for samples E and F*

where it is lowest, and then slightly increasing in value again for the remaining two sections. This same variation applies to the values for tensile strength, in pounds per square inch, but is not so marked, due to the fact that the thickness is variable, which greatly affects these values. As an illustration, considering Fig. 5, it appears that there is a large difference between sides *A* and *B* in tensile strength in pounds per square inch. Fig. 8 shows

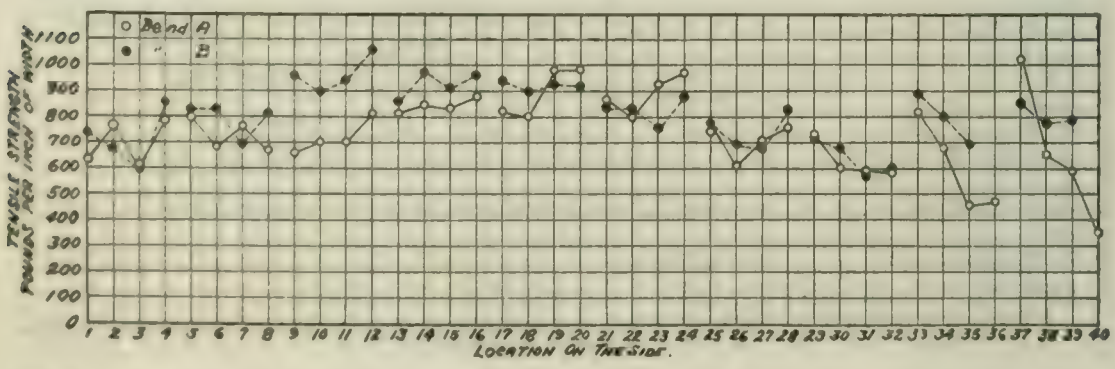


FIG. 8.—*Variation of tensile strength in pounds per inch of width over the side for samples A and B*

the values of the tensile strength, in pounds per inch of width, for these two sides, and it will be noted that there is not such a marked difference between the values as in the case of Fig. 5. The difference shown in Fig. 5 is due to the fact that the average thickness over the side was greater for one than for the other.

Thus, it is conceivable that the products of two different tanners might have equal strength per inch of width, but due to the different methods used the thickness of one tanner's leather might be considerably less or greater than that of the other tanner, and the results would be that, although the amount of fiber substance was the same, the tensile strength as expressed in pounds per

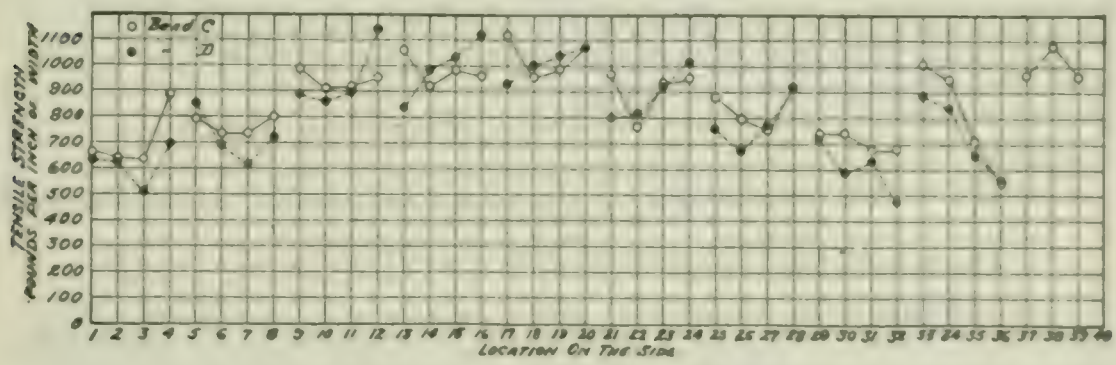


FIG. 9.—*Variation of tensile strength in pounds per inch of width over the side for samples C and D*

square inch would be quite different for the two leathers. The functions of the various parts of a harness are to withstand a definite strain or pull in tension which depends more upon the strength of the leather per inch of width than upon the strength per square inch of cross section. One tanner might furnish a thick leather of the required strength and another a thinner leather of the same strength. Both would have the same work

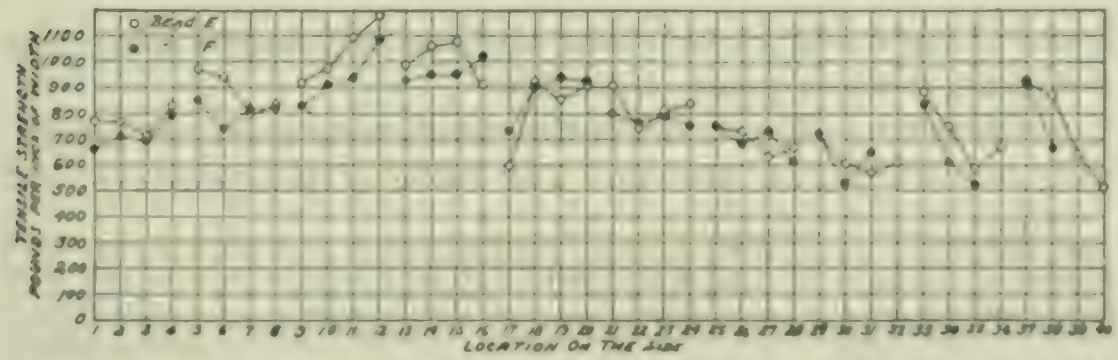


FIG. 10.—*Variation of tensile strength in pounds per inch of width over the side for samples E and F*

to do. In view of these facts, it would seem desirable for specifications to require a strength in pounds per inch of width rather than in pounds per square inch.

The graphs show that there is a great variation in the strength in pounds per square inch over the hide, and for this reason it is difficult to set a standard value. The generally accepted requirement has been 4000 pounds per square inch and these tests justify

the choice, although in the two butt-end sections of all the sides the value is somewhat less. The results also show that the strength of the more open texture, looser, long-fibered belly and shoulder portions is equal to or greater than the strength of any other

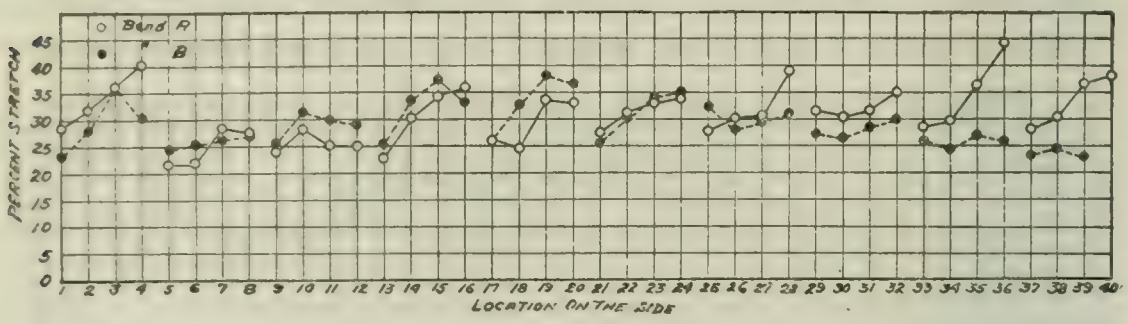


FIG. 11.—*Variation in per cent stretch over the side for samples A and B*

portions of the side. The quality of the leather from these portions, however, is inferior to the more closely fibered and firmer area extending approximately 15 inches on either side of the back-

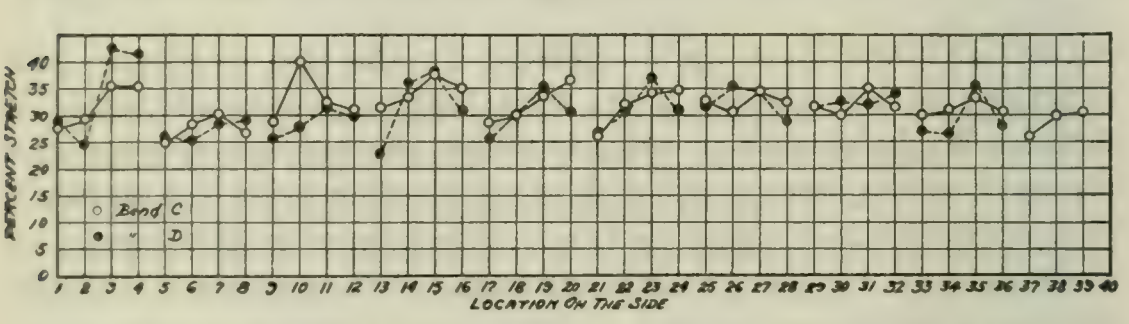


FIG. 12.—*Variation in per cent stretch over the side for samples C and D*

bone. Thus it will be seen that high tensile strength alone does not insure the best quality of leather.

(*b*) STRETCH.—The results of the stretch tests are shown graphically in Figs. 11, 12, and 13. The value of this property was

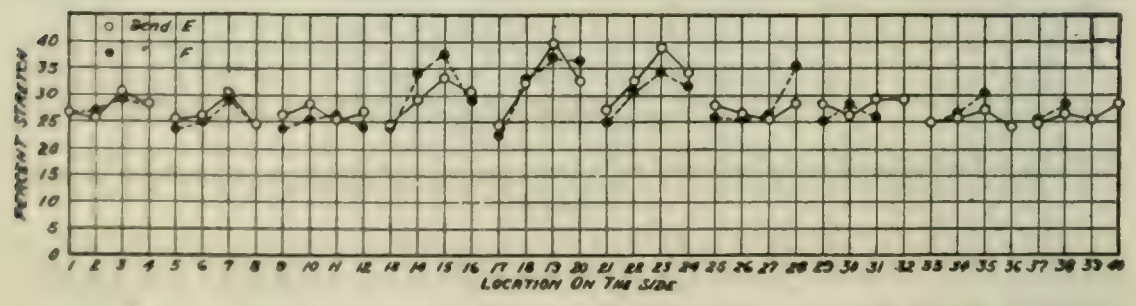


FIG. 13.—*Variation in per cent stretch over the side for samples E and F*

lowest along the backbone edge of the sides and increased toward the belly edge, although in some cases it dropped slightly in value on the extreme belly edge. An interesting fact regarding the stretch shows that in many cases it increases when the strength is

low and decreases when it is high. This does not occur in proportion to the difference in strength, but is clearly shown by the fact that the strength curves for any section of a side generally appear to be concave, while the stretch curves are more convex.

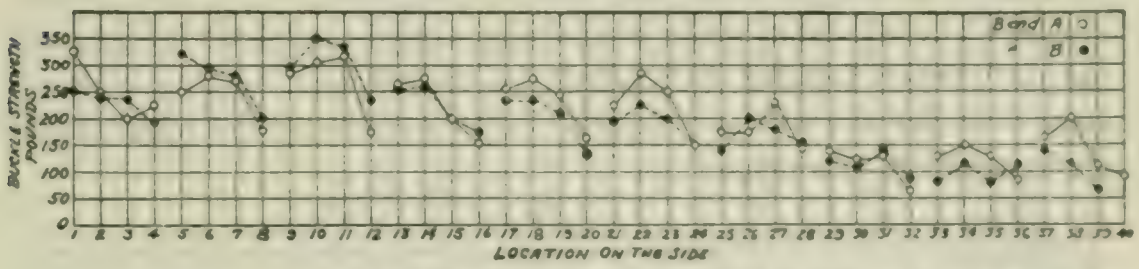


FIG. 14.—*Variation in buckle strength over the side for samples A and B*

(*c*) BUCKLE STRENGTH.—The results of the buckle strength tests are shown graphically in Figs. 14, 15, and 16. It will be seen that the value for this property is generally low on the backbone edge, increasing slightly in value toward a point near the

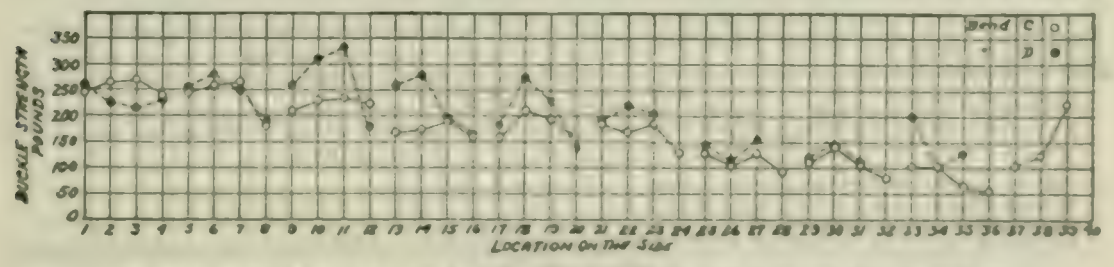


FIG. 15.—*Variation in buckle strength over the side for samples C and D*

belly edge, after which it decreases to a minimum at the belly edge for any section of four blocks running across the bend. The average value for the buckle strength for any section is greatest in the butt end and decreases steadily to the shoulder end.

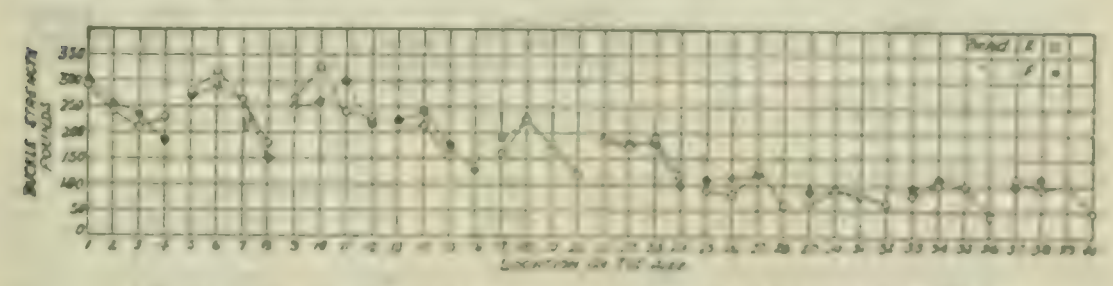

FIG. 16.—*Variation in buckle strength over the side for samples E and F*

An effort was made to establish a percentage relation between the buckle strength and tensile strength per inch of width. This relation was subject to a variation of from 10 to 50 per cent in one side, so that no satisfactory figure could be accepted as standard. The results, however, show that the belly and shoulder pro-

tions are inferior to the remaining portion of the side for use in straps which are to be used with a buckle. The best portion of a hide for this purpose, as shown by these tests, would be that included in an area about 15 inches either side of the backbone and 30 inches in length from the root of the tail. This test would not be of much value when examining samples of sides for general use as harness leather, but would be valuable in testing a lot of straps cut for use with a buckle. Table 1 gives the average values resulting from the tests.

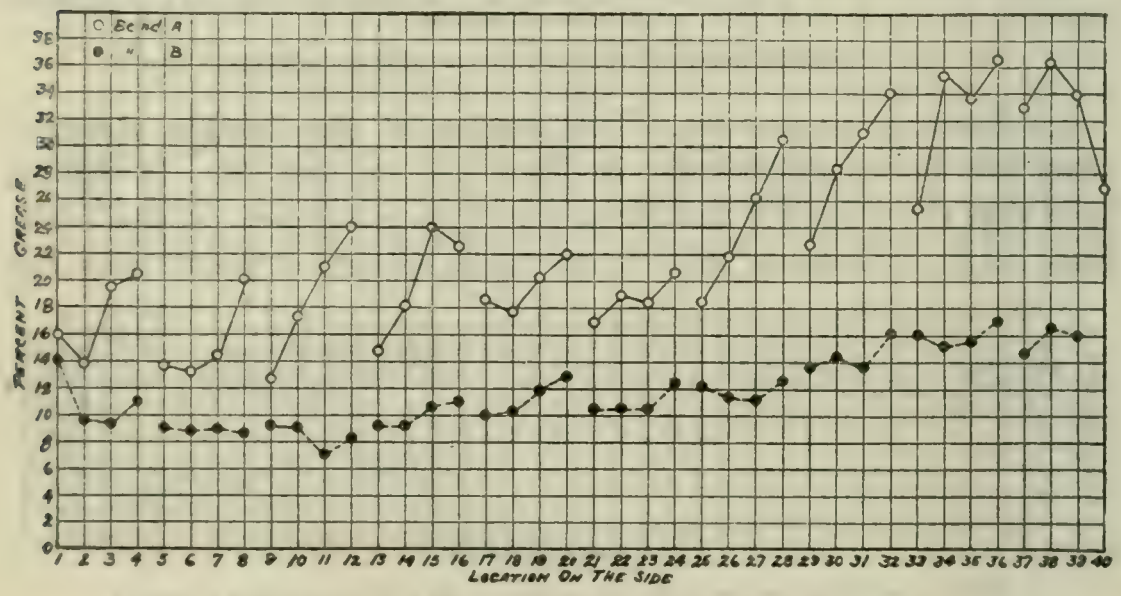


FIG. 17.—*Variation of stuffing content over the side for samples A and B*

**TABLE 1.—Average Values for Thickness, Tensile Strength, Percentage Stretch and Buckle Strength for each Side**

| Butt | Side | Thickness, inches | Tensile strength | | Percentage stretch | Buckle strength, pounds |
|---|---|---|---|---|---|---|
| | | | Pounds per inch of width | Pounds per square inch | | |
| 1 | A | 0.196 | 740 | 3835 | 30.8 | 201 |
| 1 | B | .178 | 806 | 4600 | 29.0 | 195 |
| 2 | C | .180 | 865 | 4920 | 31.6 | 170 |
| 2 | D | .198 | 810 | 4130 | 31.1 | 205 |
| 3 | E | .175 | 815 | 4705 | 28.3 | 163 |
| 3 | F | .172 | 795 | 4605 | 28.2 | 180 |

## 2. CHEMICAL TESTS

(*a*) STUFFING CONTENT.—The values for the amount of stuffing content found in each block are shown graphically in Figs. 17, 18, and 19. The average amount for any section is least at the

butt end and then gradually increases to the shoulder, where the stuffing content is greatest. The general tendency is for the stuffing content to be greatest in the more open belly and shoulder portions. In the case of all except bend *A* the average stuffing

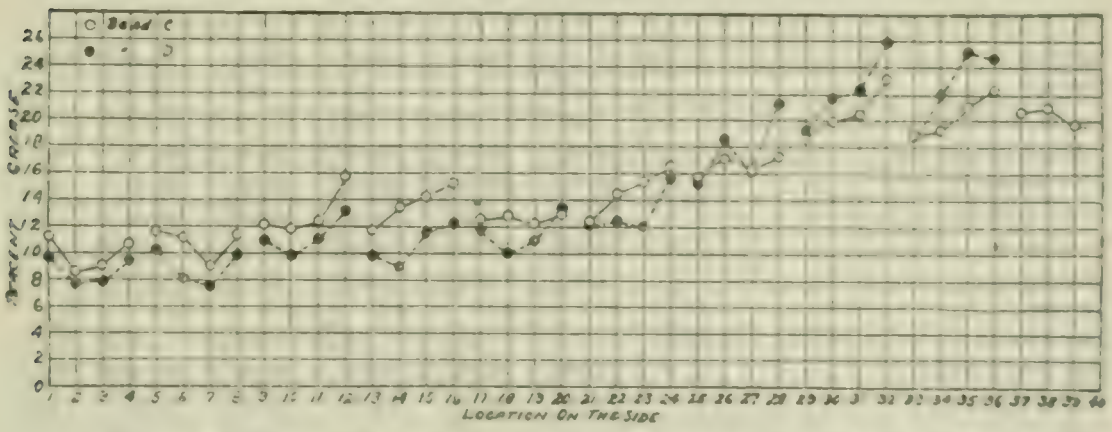

FIG. 18.—*Variation of stuffing content over the side for samples C and D*

content runs from 10 to 15 per cent and is shown to be fairly evenly distributed over the side, except in the shoulder. When a larger amount of stuffing was used, as in the case of bend *A*, the distribution over the hide was less uniform, and the greater

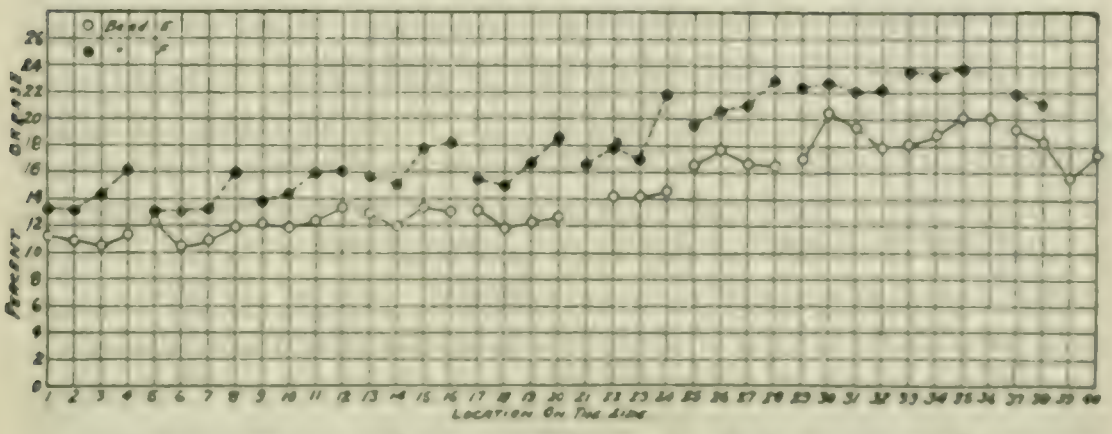

FIG. 19.—*Variation of stuffing content over the side for samples E and F*

part of the stuffing was absorbed by the belly and shoulder portions of the hide.

(*b*) COMPLETE ANALYSIS.—A complete chemical analysis was made of each side, and the results are given in Table 2.

**TABLE 2.—Results of Complete Chemical Analyses for all Sides**

[Calculated to 10 per cent moisture]

| | Butt No. 1 | | Butt No. 2 | | Butt No. 3 | |
|---|---|---|---|---|---|---|
| | Side A | Side B | Side C | Side D | Side E | Side F |
| Moisture | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 |
| Total ash | .32 | .27 | .43 | .35 | .31 | .31 |
| $MgSO_4 7H_2O$ | .23 | .23 | .21 | .22 | .23 | .22 |
| Grease | 23.35 | 10.70 | 13.30 | 11.46 | 13.72 | 15.70 |
| Hide substance | 32.74 | 39.92 | 40.24 | 39.81 | 37.32 | 36.10 |
| Water soluble | 10.05 | 10.20 | 9.88 | 10.66 | 10.92 | 9.77 |
| Nontans | 2.06 | 2.07 | 2.58 | 2.16 | 2.27 | 2.20 |
| Tans | 7.99 | 8.13 | 7.30 | 8.50 | 8.65 | 7.57 |
| Glucose | (a) | (a) | (a) | (a) | (a) | (a) |
| Insoluble ash | .12 | .14 | .14 | .14 | .14 | .22 |
| Combined tannin | 23.74 | 29.03 | 26.44 | 27.93 | 27.90 | 28.20 |
| Degree of tannage [b] | 72.51 | 72.73 | 65.71 | 70.16 | 74.93 | 78.12 |
| Acidity | .50 | .52 | .35 | .32 | .55 | .37 |

[a] None. [b] Degree of tannage is in each case calculated from the figures given in corresponding table.

### 3. COMPARISON OF PHYSICAL AND CHEMICAL TESTS

(*a*) Effect of the Amount of Stuffing Content on the Physical Properties.—The two sides *A* and *B* from the same hide were prepared to show the effect of different amounts of stuffing content on the physical properties. Side *A* contained 23.35 per cent of grease, while side *B* contained 10.70 per cent. It is apparent from Fig. 5 that side *A*, which contains the higher percentage of grease, is uniformly lower in tensile strength expressed in pounds per square inch than is side *B*. The average difference in strength is nearly 20 per cent and since the two sides are as nearly equal in quality in every respect, except grease content, as is possible to obtain it might be assumed that the difference in strength is caused by the different grease contents. The higher stuffing content in side *A*, however, caused another effect that must be considered, which was to increase materially the thickness of the side so that its average thickness throughout was 10 per cent greater than that of side *B*. Hence the cross-sectional areas of the various test pieces were greater for side *A* than for side *B*. This fact, assuming that the same breaking load would be obtained for test pieces from the same relative location on each side, would cause one test piece from side *A* to have a lower strength per unit of cross section. Thus, it would appear that about one-half, or 10 per cent, of the difference in strength indicated in Fig. 5 is due to the difference in thickness of the two sides which was caused by the different stuffing contents. The remaining 10 per cent

difference in strength may be attributed directly to the grease content.

In the case of the tensile strength in pounds per inch of width (Fig. 8) side *B* has an average value 9 per cent greater than that of side *A*. Since the tensile strength per square inch for side *B* was 20 per cent greater than that for side *A*, half of which was apparently caused by the difference in thickness of the two sides, the remaining 10 per cent can be attributed to the difference of the two sides in the strength per inch of width. The strength in pounds per inch of width is a more nearly true indication of the comparative strength of different leathers, since it does not take into account the thickness, which might vary for leathers on account of any difference in the methods of tanning and finishing by different manufacturers, and expresses the result for the same amount of original hide substance regardless of the treatment of the hide.

The effect of the grease content on the stretch was not appreciable, and the difference between the average values for the two sides was only about 3 per cent.

There did not appear to be any appreciable effect, because of the grease content, on the buckle strength. The difference between the average values for the two sides was about 3 per cent.

It can not be definitely stated from the results of these tests whether the variation in the grease content over the hide has any effect on the strength. It is more likely that any effect produced by the variation is secondary to the effect on the strength caused by the location on the hide from which a sample is taken.

(*b*) Effect of the Degree of Tannage on the Physical Properties.—Sides *C* and *D* were prepared for this test. Side *D* was tanned the longer time, but the analysis of both show that side *C* had reached that stage in the tanning process beyond which the increase in the degree of tannage is slow. This is shown by the fact that the difference in the degree of tannage figures for the two sides was approximately 5.

The tensile strength in pounds per square inch (Fig. 6) for side *C* was uniformly greater throughout than for side *D*. This result is what would be expected, since side *C*, having the lighter tannage, was relatively nearer to the raw-hide condition in which condition the strength would be greatest. The average strength, in pounds per square inch, for side *C* was approximately 20 per cent greater than for side *D*, but, as was the case with sides *A* and *B*, side *D* was also 10 per cent thicker than side *C*, thus causing its average

tensile strength in pounds per square inch to be considerably less for the same amount of original hide. The average strength per inch of width for side *C* was 7 per cent greater than for side *D*. Although the degree of tannage values for these two sides was not very different, it would appear that the lower strength of side *D* is due to the longer time in the tanning process.

The stretch of the leather did not appear to be materially affected by the different lengths of tannage, the average value for the stretch being nearly the same in both cases.

The average buckle strength for side *D* (Fig. 15) was approximately 20 per cent greater than the value for side *C*. Thus, it would appear that a long-time tannage would produce a more solid and firmer leather, which would resist a shearing action to a greater degree than a leather tanned for a shorter period of time.

(*c*) EFFECT OF ANIMAL AND MINERAL OILS ON THE PHYSICAL PROPERTIES.—Sides *E* and *F* were prepared for this test. The average tensile-strength and stretch values were nearly the same for both sides, but the average buckle strength of side *F* was approximately 10 per cent greater than the average value for side *E*. This may be on account of the fact that, although both sides were tanned for the same length of time, side *F* had a higher value for the degree of tannage. The results indicate that there is no essential effect upon the physical properties of new leather caused by the use of mineral instead of animal oils in the stuffing content.

## IV. CONCLUSIONS

Although this investigation was somewhat limited in its scope, the following general conclusions have been drawn, based upon the results obtained with the material used in these experiments:

1. That the amount of stuffing content affects the tensile strength of the leather and that there is a point beyond which the amount of stuffing content used does not add to the strength and may actually serve to decrease it.

2. That the tensile strength is greater for leather tanned a short time than for leather given a long-time tannage, and that the degree of tannage also affects the firmness of the leather, the longer-time tannage producing leather more resistant to shear when used with a buckle.

3. That the use of the type of mineral oil with which side *F* was stuffed does not affect the physical properties of new leather in a manner different than that caused by the use of cod oil.

WASHINGTON, October 27, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 161

## A PICNOMETER FOR THE DETERMINATION OF DENSITY OF MOLASSES

BY

W. B. NEWKIRK, Associate Chemist

*Bureau of Standards*

APRIL 6, 1920

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1920

# A PICNOMETER FOR THE DETERMINATION OF DENSITY OF MOLASSES

By W. B. Newkirk

The difficulty of obtaining accurate results on the density determinations of viscous liquids has long been recognized. During the past few years there has been a great increase in the quantity and value of all grades of molasses and sirups. In the determination of the value of these products for commercial purposes the density is necessarily one of the important factors. Its accurate determination in all viscous liquids is likewise of importance for scientific purposes. It has, therefore, become essential that a method be developed to determine this quantity with all possible accuracy, and it is to this end that the present work was undertaken.

The difficulties met in the accurate determination of the density of molasses are due to (1) high viscosity, (2) included gases, and (3) dissolved gases.

As a result of the high viscosity, the use of hydrometers is prevented, and the thorough mixing or intermingling of the various components of the batch or sample of molasses is made difficult. Obviously, in materials of this character a representative sample can not be obtained without vigorous agitation, which causes the entrainment or inclusion of large amounts of air. Finally, the viscosity retards the escape of the entrained or included air.

The effects of included air upon the density of the liquor are too evident to need discussing. The removal of the dissolved gases before taking the density may in some cases be essential and in others not.

It was decided to use the picnometer or specific-gravity bottle as a starting point in the development of an improved procedure. The picnometer of Johnson and Adams [1] was accepted as the most accurate type to control the volume. In this bottle the volume is fixed by an optically flat disk, seating on an optically

[1] Jour. of Am. Chem. Soc., 34, p. [illegible], 1912.

flat plane ground on an enlarged rim at the top of the bottle. The fact that it is not necessary to use a lubricant on this joint, the absence of errors caused by dirt lodging in the customary ground stopper, and the greater ease with which the surfaces can be brought into contact when using a viscous material, permit great accuracy in fixing the volume. Johnson and Adams found that the volume could be reproduced to within 0.2 mg of water, and the author found similar accuracy.

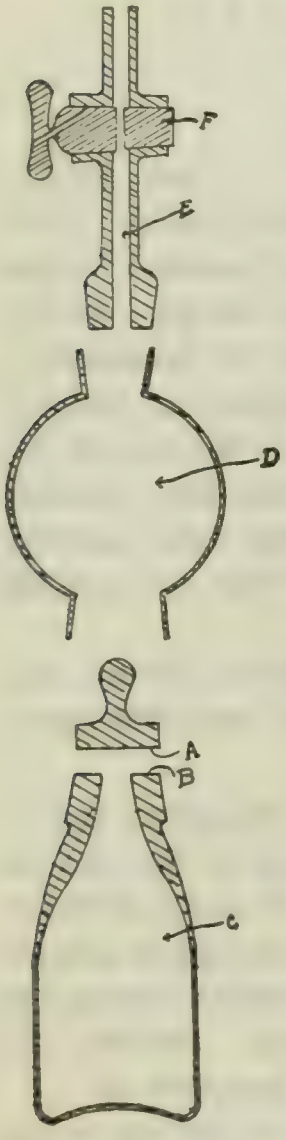


FIG. 1.—*Form of picnometer used*

Any known method of removing the included gases causes considerable foaming. This necessitates the removal of the air before filling or the accommodation of this foam in the picnometer design. In an effort to meet this difficulty a large expansion chamber, equipped with a ground joint and fitted over the top of the bottle, has been described by an anonymous writer.[1] This permitted the molasses to expand into the chamber while deaerating, and then as the gas rose to the surface the air-free molasses filled the bottle. When the bottle was full, the volume of molasses could be fixed.

Investigations at this Bureau established the fact that the removal of gases was best effected by the use of a vacuum. In order to permit this to be done as readily and effectively as possible, an improved picnometer, shown in Fig. 1, was designed.

It consists of a bottle, *C*, fitted with an enlargement at the top, *B*, ground optically flat and closed off by another optical flat, *A*. An expansion chamber, *D*, is ground to the bottle and fitted with a vacuum connection, *E*. To avoid loss of water due to evaporation under reduced pressure, the connecting tube is fitted with a stopcock, *F*, so that when the proper vacuum has been reached the apparatus can be closed off from the vacuum source. With this provision the volume to be filled with water vapor is very small and the amount of water evaporated will be negligible. The bottle is so shaped as to have a smooth gradual slope to the top, so that the bubbles will rise with the least effort to the expan-

[1] Anonymous—International Sugar Jour., 15, p. 489; 1913.

sion chamber. It has thick walls over the neck, so that it can be readily handled without changing the temperature or volume by heat transmitted to the flask by the fingers. The joints of the expansion chamber, vacuum connection, and stopcock are ground to an accurate fit. Since it is unnecessary to employ a vacuum with a pressure lower than the vapor pressure of molasses at room temperature, it is entirely practicable to utilize the sample under test to lubricate and seal all the ground joints. Needless to say, this is an important advantage.

In using the picnometer, the expansion chamber, after lubrication of all joints with molasses, is placed on the bottle. The molasses to be analyzed is flowed into the bottle and into the expansion chamber until the latter is about one-third full. The vacuum line is then connected and the pressure reduced until the gas expands to visible bubbles. The apparatus is immediately closed off by turning the stopcock, *F*, and the whole placed in the thermostat for accurate work or in the balance case for control work. When all the bubbles have collected in the expansion chamber and the temperature has reached equilibrium, the volume is fixed with the plate after removing the expansion chamber. It is then wiped and weighed.

The densities are determined by correcting the weights to vacuo and comparing to the weight of an equal volume of water at 4° C in vacuo. They are reported in degrees Brix,[1] according to Circular 44 of this Bureau.

In the present investigation, two methods for de-aerating were studied:

1. Heating.—This reduces the viscosity and expands the gases, causing the separation to take place more quickly.

2. The Application of Vacuum.—This expands the gases, causing a rapid separation to take place.

The use of heat was found to cause considerable decomposition of an unknown character, as will be seen from the following experiments:

Experiment 1.—The density was determined after filling. Brix found, at 20° C, 76.41°.

Experiment 2.—After experiment No. 1 the picnometer was allowed to stand without refilling, the expansion chamber in place and a third full, for 24 hours. In removing the expansion cham-

[1] Degrees Brix is the density of a pure-sugar solution expressed as the percentage by weight of sugar present in the solution. The comparison of density and degrees Brix is tabulated in Table 31 Circular 44, of the Bureau of Standards.

ber care was taken to save the extra molasses in the chamber for the next experiment. After standing 24 hours the density was determined. Brix found, at 20° C, 76.91°.

EXPERIMENT 3.—The picnometer was subjected to vacuum without refilling and with the same molasses in the expansion chamber. The vacuum applied was equal to 200 mm mercury and was held for 12 hours, after which the expansion chamber was removed with the same care as in experiment No. 2. The density was again determined. Brix found, at 20° C, 76.96°.

EXPERIMENT 4.—The picnometer again, with the same molasses and without refilling, was, with the expansion chamber and its same molasses in place, immersed in a water bath held at 80° C for a period of two hours. It was brought to 20° C, and the density was again determined and was found considerably lower than experiment No. 3. Brix found, at 20° C, 76.66°.

*Experiment 5.*—The picnometer was refilled with the original molasses and, with the expansion chamber in place, was subjected to the same conditions as No. 3, namely, 200 mm vacuum at room temperature for 12 hours. The density found checked satisfactorily with that found in No. 3. Brix found, at 20° C, 77.04°. The data are summarized in Table 1.

It is seen that in experiment No. 4, in which heat was used to aid the deaerating, the density is considerably lower than those found in experiments 2, 3, or 5, and is not in agreement with them. It is evident that the use of heat should be avoided.

**TABLE 1**

| Experiment No. | Time standing | Temperature | Vacuum | Degrees Brix at 20° C |
|---|---|---|---|---|
| | Hours | °C | Millimeters | |
| 1 | (a) | 24 | (a) | 76.41 |
| 2 | 24 | 24 | (a) | 76.91 |
| 3 | 12 | 22 | 200 | 76.96 |
| 4 | 2 | 70 | (a) | 76.66 |
| 5 | 12 | 20 | 200 | 77.04 |

[a] None.

The reproducibility obtained is shown by the data given in Table 2. The experiments were conducted as outlined in describing the use of the picnometer. The joints were lubricated with molasses and the bottle filled and the expansion chamber one-third filled with the molasses, a vacuum of 200 mm was applied and the picnometer sealed off. After standing 12 hours at room

temperature, it was placed in a thermostat held at 20° C until equilibrium was established. The volume was then fixed and the weighing immediately made.

**TABLE 2.—Density Determinations of Molasses**

| Material | Duplicate 1 | Duplicate 2 |
|---|---|---|
| | Degrees Brix | Degrees Brix |
| Black-strap molasses A | 76.96 | 77.04 |
| Black-strap molasses B | 76.91 | 76.91 |
| Beet molasses | 81.40 | 81.37 |
| Black-strap molasses C | 76.77 | 76.76 |
| Black-strap molasses D | 77.41 | 77.41 |
| Black-strap molasses E | 68.70 | 68.71 |

We may, then, say that the individual accidental error is within one-tenth of 1° Brix, and therefore considerably better than hitherto attainable. The general run of determinations will check to within a few hundredths of 1° Brix. In summarizing, it may be stated that a new picnometer design has been developed which permits greater accuracy in density determinations of molasses than has been possible heretofore. A method of removing the entrained gases is proposed which does not have the bad features of heating or dilution. Heating is shown to have a deleterious effect in density determinations. The accidental error is shown to be small and probably smaller than the accuracy with which a representative sample of a given molasses can be obtained.

WASHINGTON, December 18, 1919.

DEPARTMENT OF COMMERCE

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## No. 162

# EXTRACTION OF RUBBER GOODS

BY

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B. L. GONYO, Laboratory Assistant
*Bureau of Standards*

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# EXTRACTION OF RUBBER GOODS[1]

By S. W. Epstein and B. L. Gonyo

CONTENTS


| | | Page |
|---|---|---|
| 1. | Introduction | 3 |
| 2. | Preliminary experiments | 3 |
| 3. | Discussion of preliminary results | 8 |
| 4. | Effect of mixed solvent on free sulphur | 10 |
| 5. | Extraction of high-grade stocks | 11 |
| 6. | Effect of solvents on rubber | 11 |
| 7. | Summary | 13 |


## 1. INTRODUCTION

In rubber analysis, where rubber is determined indirectly as the difference between 100 per cent and the sum of the organic extracts, ash, and total sulphur, it is important that the extracts represent as much as possible of the organic materials which were added to the rubber batch and which are not determined separately. Those who have tried to extract glue from a vulcanized compound containing it, by means of boiling water, know how tenaciously rubber clings to certain admixed materials. In this work it was our intention to ascertain as far as possible how much, if any, soluble organic material is retained in a compound after it has been extracted with acetone for eight hours and chloroform for four hours in the usual way.

## 2. PRELIMINARY EXPERIMENTS

For this purpose we chose a cheap rubber mixture containing mineral rubber and pine tar and extracted it successively as follows:

Experiment I

| Extracts | Hours | Per cent |
|---|---|---|
| (a) Acetone extract | 8 | 10.56 |
| (b) Chloroform extract | 4 | 2.00 |
| (c) Mixture of chloroform and acetone | 4 | 2.00 |
| Total | | 14.56 |

[1] Paper read before the rubber division of the American Chemical Society at its Philadelphia meeting, September, 1919.

**Experiment II**

| Extracts | Hours | Per cent |
|---|---|---|
| (a) Acetone extract | 8 | 10.16 |
| (b) Chloroform extract | 4 | 2.0 |
| (d) Mixture of carbon bisulphide and acetone | 4 | 3.5 |
| Total | | 15.66 |

Extracts (*c*) and (*d*), 2.0 and 3.5 per cent, respectively, are not removed in the standard procedure and therefore give us the first indication that organic material is retained in the rubber after the usual extractions have been carried out.

The residues from Experiments I and II were now digested in 25 cc of cresol (B. P. 195°) for four hours at 165° C. The solution obtained was then diluted with petroleum ether and allowed to stand over night. In the morning it was filtered upon a Gooch crucible and washed thoroughly with petroleum ether and boiling benzene. The filtrate contained vulcanized rubber, while the pad presumably retained only the fillers. Our experience with cresol as a solvent for vulcanized rubber has shown that there is on the pad no material soluble in acetone or chloroform when a compound containing only rubber, sulphur, and inorganic filler is treated with cresol in the manner given above. However, when this compound, which contained pine tar and mineral rubber, was treated in the same way, acetone extracted (I) 1.6 per cent and (II) 1.12 per cent, respectively, from the material on the pad. These figures represent a part of these organic additions which remained in the rubber after it was extracted.

This extract seems to have been released by the dissolution of the rubber in the compound. Further, when the pad was washed with hot 10 per cent hydrochloric acid and water, and then extracted with acetone again, the following extracts were obtained: (I) 3.28 per cent and (II) 3.88 per cent. In this case this material was retained by the fillers themselves and was released when they were dissolved out. A mixture of 50 per cent acetone and 50 per cent carbon bisulphide extracted (I) 1.64 per cent, and (II) 0.92 per cent additional

Arranging the extracts in the order in which they were obtained, our results are:

**Experiment I**

| Extracts | Per cent | |
|---|---|---|
| Acetone extract on original sample | 10.56 | |
| Chloroform extract on residue | 2.0 | A |
| Additional extract obtained by means of a mixture of chloroform and acetone | 2.0 | B |
| Acetone extract on the total fillers which were separated from the rubber by means of cresol | 1.6 | |
| Acetone extract on the residue after it had been washed with 10 per cent hydrochloric acid | 3.3 | C |
| Additional extract obtained by washing with a mixture of carbon bisulphide and acetone | 1.6 | |
| Total extracts | 21.1 | |

Of this total of 21.1 per cent of extractable material only 12.56 per cent is obtained in the regular procedure, while B and C, totaling 8.5 per cent, are left behind and are therefore reported as rubber hydrocarbon.

**Experiment II**

| Extracts | Per cent |
|---|---|
| Acetone extract on the original sample | 10.16 |
| Chloroform extract on the residue | 2.00 |
| Additional extract obtained by means of a mixture of carbon bisulphide and acetone | 3.5 |
| Acetone extract on the total fillers which were separated from the rubber by means of cresol | 1.12 |
| Acetone extract on the residue after it had been washed with 10 per cent hydrochloric acid | 3.88 |
| Additional extract obtained by washing with a mixture of carbon bisulphide and acetone | .92 |
| Total extracts | 21.58 |

In this case, of the total of 21.6 per cent of extractable material only 12.2 per cent is obtained in the regular procedure, while B and C, totaling 9.4 per cent, are left behind.

It is easy to see, therefore, that in the case of cheap compounds the figure for rubber obtained by the "difference" method can not be at all reliable because of the retention of the organic material extracted as under B and C.

As long as the ashing method is used, it is clear that an accurate figure for rubber can not be expected for this reason. At best it can be but an approximation.

In connection with this work attention is drawn to the use of mixed solvents, such as acetone-chloroform and acetone-carbon bisulphide, which were used above. It was found with Experiment I that a mixture of chloroform and acetone extracted 2 per cent in four hours after the usual acetone and chloroform extractions had been run. Likewise, with Experiment II a mixture of carbon bisulphide and acetone extracted 3.5 per cent in the same

way. Such additional extracts, although they do not remove all of the material, nevertheless make the approximation closer. Considerable work has been done on the effectiveness of such mixed solvents.

When washing the pad through which a cresol solution of rubber had been filtered, it was discovered that usually a second extract of considerable weight could be obtained by subjecting the pad to alternate washings with acetone and carbon bisulphide after it was presumably free from all extractable material. We found that the coloration due to material being extracted out lasted only a short time, but reappeared on changing to the other solvent. The effectiveness of such alternate washings we believed to have been the result of a mixture of the solvents which was formed on the pad by the last few drops of the one solvent with the first few of the second which was being poured on. To prove this we tried washing with a mixture of equal volumes of the two solvents. The solvent power of such a mixture we found to be surprising. After washing with this mixture it was found that no further extract could be obtained by the alternating method mentioned above. This result of washing alternately with two solvents was noticed when we were working on the determination of free carbon in rubber goods, but we did not at that time grasp its significance. In this determination the rubber sample is treated with hot nitric acid, this solution filtered upon a Gooch, and the pad washed with nitric acid, acetone, and chloroform. It was found that this same pad, presumably free from extractable material, gave further extracts in many cases when the solvents were alternated.

Finding that such mixtures as acetone-carbon bisulphide and acetone-chloroform were more effective than the simple solvents in washing residues on Gooch pads, it occurred to us that if a constant boiling mixture of these solvents could be obtained this mixture might find application in the extraction of rubber goods in the Soxhlet.

Ryland [2] found that a mixture of 55 per cent carbon bisulphide and 45 per cent acetone by volume has a constant boiling point of 39.25° C.; likewise a mixture of 68 per cent chloroform and 32 per cent acetone by volume boils constantly at 64.7° C. Accordingly it was decided to extract samples of cheap rubber with acetone for eight hours and then with such a constant boiling mixture, and compare the weight of extract so obtained with that obtained by means of pure carbon bisulphide or pure chloroform. The following is a record of our work:

[2] Ryland, Jour. Amer. Chem. Soc., 22, p. 384; 1899. See also Young, Fractional Distillation, pp. 68 and 69.

**TABLE 1.—Extracts Obtained From Low-Grade Mixings**

| Sample | Acetone extract eight hours | Chloroform extract on acetone extracted sample four hours | Carbon bisulphide extract on acetone extracted sample four hours | 55 per cent carbon bisulphide, 45 per cent acetone on acetone extracted sample four hours | 68 per cent chloroform, 32 per cent acetone on acetone extracted sample four hours | Total | Sum of the extracts |
|---|---|---|---|---|---|---|---|
| | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | |
| | 9.8 | 2.0 | | | | 11.8 | Acetone extract + chloroform extract |
| | 9.9 | | 1.8 | | | 11.7 | Acetone extract + carbon-bisulphide extract |
| I | 9.8 | | | 6.4 | | 16.2 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 9.8 | | | | 6.8 | 16.6 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 10.3 | 3.4 | | | | 13.7 | Acetone extract + chloroform extract |
| | 10.3 | | 1.9 | | | 12.2 | Acetone extract + carbon-bisulphide extract |
| II | 10.4 | | | 4.5 | | 14.9 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 10.3 | | | | 4.2 | 14.5 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 15.3 | 3.7 | | | | 19.0 | Acetone extract + chloroform extract |
| | 15.3 | | 3.2 | | | 18.5 | Acetone extract + carbon-bisulphide extract |
| III | 15.3 | | | 6.5 | | 21.8 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 15.3 | | | | 4.6 | 19.9 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 13.3 | 2.2 | | | | 15.5 | Acetone extract + chloroform extract |
| | 13.3 | | 1.7 | | | 15.0 | Acetone extract + carbon-bisulphide extract |
| IV | 13.3 | | | 4.3 | | 17.6 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 13.3 | | | | 2.9 | 16.2 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 9.1 | .8 | | | | 9.9 | Acetone extract + chloroform extract |
| | 8.7 | | 1.1 | | | 9.8 | Acetone extract + carbon-bisulphide extract |
| V | 9.2 | | | 3.2 | | 12.4 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 9.2 | | | | 1.5 | 10.7 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 13.7 | .5 | | | | 14.2 | Acetone extract + chloroform extract |
| | 13.7 | | .5 | | | 14.2 | Acetone extract + carbon-bisulphide extract |
| VI | 13.7 | | | 2.4 | | 16.1 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 13.7 | | | | 4.0 | 17.7 | Acetone extract + 68 per cent chloroform-32 per cent acetone extract |
| | 7.7 | .6 | | | | 8.3 | Acetone extract + chloroform extract |
| VII | 7.7 | | .4 | | | 8.1 | Acetone extract + carbon-bisulphide extract |
| | 7.7 | | | 2.5 | | 10.2 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 4.7 | .6 | | | | 5.3 | Acetone extract + chloroform extract |
| VIII | 4.7 | | .6 | | | 5.3 | Acetone extract + carbon-bisulphide extract |
| | 4.7 | | | 2.2 | | 6.9 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 12.6 | 1.5 | | | | 14.1 | Acetone extract + chloroform extract |
| IX | 12.7 | | 1.2 | | | 13.9 | Acetone extract + carbon-bisulphide extract |
| | 13.0 | | | 1.8 | | 14.8 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 9.1 | .7 | | | | 9.8 | Acetone extract + chloroform extract |
| X | 9.1 | | .5 | | | 9.6 | Acetone extract + carbon-bisulphide extract |
| | 9.1 | | | .9 | | 10.0 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |
| | 6.3 | .6 | | | | 6.9 | Acetone extract + chloroform extract |
| XI | 6.3 | | .5 | | | 6.8 | Acetone extract + carbon-bisulphide extract |
| | 6.3 | | | 1.1 | | 7.4 | Acetone extract + 55 per cent carbon bisulphide-45 per cent acetone extract |

### 3. DISCUSSION OF PRELIMINARY RESULTS

It is plain from the figures tabulated here that chloroform is slightly better than carbon bisulphide as a solvent for extracting rubber; while the constant boiling mixture, whether it be 55 per cent carbon bisulphide and 45 per cent acetone, or 68 per cent chloroform and 32 per cent acetone, is certainly a much more efficient solvent than either carbon bisulphide or chloroform. These mixtures removed extracts that in some cases were astonishing. In Case I, carbon bisulphide extracted 1.82 per cent, while the mixtures extracted 6.4 and 6.8 per cent, respectively. Case VI is even more striking, for carbon bisulphide removed only 0.43 per cent, while the mixture of 55 per cent carbon bisulphide and 45 per cent acetone removed 2.54 per cent.

Further, these results indicate that one extraction with a constant boiling mixture may take the place of the two extractions, namely, acetone for eight hours followed by chloroform for four hours, according to common practice in the rubber laboratory to-day. The following work was carried out in order to ascertain whether such a substitution would be advisable. The mixture used in the work was made by distilling a mixture of 55 per cent by volume of carbon bisulphide and 45 per cent by volume of acetone over copper at a temperature of 39.25° C. The solvent therefore contained no sulphides or free sulphur, so that sulphur determined in the extracts could not be attributed to the solvent. Likewise, the mixture of 68 per cent by volume of chloroform and 32 per cent by volume of acetone was freshly distilled and contained no sulphur.

**TABLE 2.—Extracts and Sulphur Obtained on Low-Grade Rubber Mixings**

| Sample | A $(CH_3)_2CO$ extract eight hours | | B $CHCl_3$ extract after A four hours | | C $CS_2$-$(CH_3)_2CO$ extract after A four hours | | D $CS_2$-$(CH_3)_2CO$ on original sample eight hours | | E $CHCl_3$-$(CH_3)_2CO$ on original sample nine hours | | F Total | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ext. | S | Ext. | S | Ext. | S | Ext. | S | Ext. | S | Ext. | S | How obtained |
| XII | 11.7 | | 4.6 | | | | | | | | 16.3 | | A + B |
| | | 1.23 | | | | | | | | | | 1.23 | Free S in A |
| | 11.9 | | | | 5.2 | | | | | | 17.1 | | A + C |
| | | 1.04 | | | | 0.07 | | | | | | 1.11 | Free S in A + C |
| | | | | | | | 16.9 | | | | 16.9 | | D |
| | | | | | | | | 1.26 | | | | 1.26 | Free S in D |
| XIII | 10.9 | | 2.5 | | | | | | | | 13.4 | | A + B |
| | | .82 | | | | | | | | | | .82 | Free S in A |
| | 10.9 | | | | 3.0 | | | | | | 13.9 | | A + C |
| | | .65 | | | | .16 | | | | | | .81 | Free S in A + C |
| | | | | | | | 15.4 | | | | 15.4 | | D |
| | | | | | | | | 1.14 | | | | 1.14 | Free S in D |
| | | | | | | | | | 16.7 | | 16.7 | | E |
| | | | | | | | | | | 1.0 | | 1.0 | Free S in E |
| XIV | 9.5 | | 2.1 | | | | | | | | 11.6 | | A + B |
| | | .8 | | | | | | | | | | .8 | Free S in A |
| | 9.3 | | | | 4.5 | | | | | | 13.8 | | A + C |
| | | .78 | | | | .04 | | | | | | .82 | Free S in A + C |
| | | | | | | | 13.2 | | | | 13.2 | | D |
| | | | | | | | | 1.12 | | | | 1.12 | Free S in D |
| | | | | | | | | | 14.6 | | 14.6 | | E |
| | | | | | | | | | | .91 | | .91 | Free S in E |
| XV | 20.7 | | 7.9 | | | | | | | | 28.6 | | A + B |
| | | .51 | | 0.15 | | | | | | | | .66 | Free S in A + B |
| | 21.5 | | | | 8.0 | | | | | | 29.5 | | A + C |
| | | .39 | | | | .06 | | | | | | .45 | Free S in A + C |
| | | | | | | | 20.4 | | | | 20.4 | | D |
| | | | | | | | | .60 | | | | .60 | Free S in D |
| | | | | | | | | | 31.1 | | 31.1 | | E |
| | | | | | | | | | | .48 | | .48 | Free S in E |
| XVI | 12.5 | | 3.3 | | | | | | | | 15.8 | | A + B |
| | | 2.15 | | .06 | | | | | | | | 2.21 | Free S in A + B |
| | 12.4 | | | | 3.5 | | | | | | 15.9 | | A + C |
| | | 2.0 | | | | .07 | | | | | | 2.07 | Free S in A + C |
| | | | | | | | 17.6 | | | | 17.6 | | D |
| | | | | | | | | 2.09 | | | | 2.09 | Free S in D |
| | | | | | | | | | 18.6 | | 18.6 | | E |
| | | | | | | | | | | 2.10 | | 2.10 | Free S in E |
| XVII | 20.5 | | 7.2 | | | | | | | | 27.7 | | A + B |
| | | .53 | | .10 | | | | | | | | .63 | Free S in A + B |
| | 20.4 | | | | 7.8 | | | | | | 28.2 | | A + C |
| | | .58 | | | | .06 | | | | | | .64 | Free S in A + C |
| | | | | | | | 28.4 | | | | 28.4 | | D |
| | | | | | | | | .12 | | | | .12 | Free S in D |
| XVIII | 15.9 | | 1.2 | | | | | | | | 17.1 | | A + B |
| | | 1.74 | | .06 | | | | | | | | 1.80 | Free S in A + B |
| | 15.7 | | | | 1.9 | | | | | | 17.6 | | A + C |
| | | 1.53 | | | | .09 | | | | | | 1.62 | Free S in A + C |
| | | | | | | | 17.7 | | | | 17.7 | | D |
| | | | | | | | | 4.13 | | | | 4.13 | Free S in D |
| XIX | 21.4 | | 2.9 | | | | | | | | 24.4 | | A + B |
| | | .6 | | .03 | | | | | | | | .63 | Free S in A + B |
| | 21.6 | | | | 2.1 | | | | | | 23.7 | | A + C |
| | | .82 | | | | .06 | | | | | | .88 | Free S in A + C |
| | | | | | | | 24.1 | | | | 24.1 | | D |
| | | | | | | | | .91 | | | | .91 | Free S in D |

**TABLE 3.—Comparison of Extracts Obtained by $CS_2$—$(CH_3)_2CO$, in 12 Hours Extraction on Low-Grade Rubber Mixings with (A+B) and (A+C), Carried out as in Table 2**

| Sample | Ext. | S | Remarks |
|---|---|---|---|
| XX | 20.0 | ..... | Acetone extract+chloroform extract—(A+B) |
| | ..... | 0.63 | Free S in extracts |
| | 21.2 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .64 | Free S in the extracts |
| | 20.5 | ..... | Extract obtained by the use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | .77 | Free S in this extract |
| XXI | 19.8 | ..... | Acetone extract +chloroform extract—(A+B) |
| | ..... | .66 | Free S in the extracts |
| | 20.0 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .77 | Free S in the extracts |
| | 20.3 | ..... | Extract obtained by the use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | 1.07 | Free S in this extract |
| XXII | 16.1 | ..... | Acetone extract+chloroform extract—(A+B) |
| | ..... | .21 | Free S in the acetone extract |
| | 16.1 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .28 | Free S in the extracts |
| | 16.7 | ..... | Extract obtained by use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | .24 | Free S in this extract |
| XXIII | 13.8 | ..... | Acetone extract+chloroform extract—(A+B) |
| | ..... | .26 | Free S in the acetone extract |
| | 14.2 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .28 | Free S in the extracts |
| | 14.2 | ..... | Extract obtained by use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | .26 | Free S in this extract |
| XXIV | 18.1 | ..... | Acetone extract+chloroform extract—(A+B) |
| | ..... | .12 | Free S in the extracts |
| | 17.5 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .14 | Free S in the extracts |
| | 17.9 | ..... | Extract obtained by use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | .14 | Free sulphur in this extract |
| XXV | 9.8 | ..... | Acetone extract+chloroform extract—(A+B) |
| | ..... | .10 | Free S in the extracts |
| | 9.6 | ..... | Acetone extract+55 per cent carbon bisulphide-45 per cent acetone extract—(A+C) |
| | ..... | .12 | Free S in the extracts |
| | 9.5 | ..... | Extract obtained by use of 55 per cent carbon bisulphide-45 per cent acetone on original sample for 12 hours |
| | ..... | .14 | Free S in this extract |

### 4. EFFECT OF MIXED SOLVENT ON FREE SULPHUR

A study of the above results reveals: (1) That a small amount of sulphur, usually less than 0.1 per cent, is extracted by the chloroform; (2) that about the same amount of sulphur is extracted by the mixture of 55 per cent carbon bisulphide and 45 per cent acetone, when this mixture is used in place of chloroform; (3) that either mixture extracts from the original sample, in 8 hours, as much or more material than the sum of the extracts obtained by the 8-hour acetone extraction and the 4-hour chloroform extraction (samples XIII and XIV are notable examples of the greater extracts that are sometimes obtained by the use of

the mixed solvents); (4) that either mixture extracts from the original sample, in 8 hours, as much or more material than the sum of the extracts obtained by an 8-hour extraction with acetone and a 4-hour extraction with a mixture of 55 per cent carbon bisulphide and 45 per cent acetone; (5) that the free sulphur present in the extracts obtained by the use of the mixtures is usually from 0.1 to 0.3 per cent higher than the amount present in the acetone extract; (6) that there seems to be no advantage in extracting 12 hours or longer with the mixed solvents, since, as shown in Table 3, the results are relatively the same after 12 hours as after 8 hours; (7) that the mixture of carbon bisulphide and acetone does not decompose during the extraction to liberate sulphur or sulphur compounds and in this way affect the free sulphur determination; (8) that the mixture of 68 per cent chloroform and 32 per cent acetone produces heavier extracts than that of 55 per cent carbon bisulphide and 45 per cent acetone.

### 5. EXTRACTION OF HIGH-GRADE STOCKS

The next step in the work was to determine the effect of the mixed solvents on high-grade stocks for the purpose of possibly being able to determine what varying solution effects they would have on vulcanized rubber. Four compounds containing A–70 per cent, B–85 per cent, C–95 per cent, and D–45 per cent, respectively, of rubber were extracted in eight hours with acetone and four hours with chloroform, and then one was subjected to four hours additional extraction with chloroform, another to four hours with 55 per cent carbon bisulphide and 45 per cent acetone, and a third to four hours with 68 per cent chloroform and 32 per cent acetone, with the following results:

| Sample | Process | A 70 per cent rubber | B 85 per cent rubber | C 95 per cent rubber | D 45 per cent rubber |
|---|---|---|---|---|---|
| 1 | Extract obtained by four hours additional extraction with chloroform | [illegible] | 0.37 | 0.59 | 0.25 |
| 2 | Extract obtained by four hours additional extraction with 68 per cent chloroform and 32 per cent acetone | .63 | .69 | 1.23 | .50 |
| 3 | Extract obtained by four hours additional extraction with 55 per cent carbon bisulphide and 45 per cent acetone | .65 | .22 | .21 | .00 |

### 6. EFFECT OF SOLVENTS ON RUBBER

All three solvents dissolve vulcanized rubber to an extent which seems to depend upon how heavily it is compounded. It is interesting to note that the mixture of 68 per cent chloroform and 32

per cent acetone exhibits this ability to dissolve rubber to a marked extent. The rubber dissolved by it in the above is nearly twice that dissolved by pure chloroform. On the other hand, the mixture of 55 per cent carbon bisulphide and 45 per cent acetone hardly exhibits this ability at all, so that the rubber dissolved by it is inappreciable as compared with that dissolved by chloroform or the mixture of chloroform and acetone. Obviously, this is a point in favor of the use of the mixture of 55 per cent carbon bisulphide and 45 per cent acetone. The point is well borne out when high-grade stocks are used to compare the extracts obtained by acetone, chloroform, and the mixture of carbon bisulphide and acetone.

| Sample | Percentage of rubber | Combined extract obtained by extraction for eight hours with acetone and four hours with chloroform | | Extract obtained by extraction for eight hours with a mixture of 55 per cent carbon bisulphide and 45 per cent acetone | |
|---|---|---|---|---|---|
| | | Extract | Free sulphur | Extract | Free sulphur |
| E | 45 | 2.40 | 0.72 | 2.0 | 0.71 |
| F | 45 | 2.7 | .64 | 1.9 | .63 |
| G | 75 | 4.5 | .37 | 4.1 | .38 |
| H | 45 | 2.7 | 1.7 | 1.7 | 1.8 |
| I | 85 | 4.3 | .82 | 3.6 | .76 |

The results obtained by the acetone-carbon bisulphide mixture on these high-grade compounds are in every case lower than the sum of the acetone and chloroform extracts, as would be expected from the work carried out on samples A, B, C, and D. The figures for free sulphur are also in accordance with previous statements given here.

It is evident, therefore, that it is highly advantageous to use the mixture of carbon bisulphide and acetone to take the place of acetone and chloroform, because of this less active solvent effect upon rubber, as shown.

Before recommending the adoption of this mixed solvent a few words must be said about deterioration of the solvent and blank extracts that will form in it. It was found that the freshly distilled mixture would give no blank and at the end of two weeks would still give no blank. However, at the end of a month's storage 75 cc of the mixture would give a residue which, although it contained no sulphur, yet weighed up to 0.006 g. Therefore it is advised that, where the mixture is being used in large quantities for routine analysis, it be redistilled over copper every week. Where it is used only occasionally it should be mixed up fresh and distilled before using.

## 7. SUMMARY

1. Extraction for 8 hours with acetone followed by 4 hours extraction with chloroform does not remove all soluble material from some rubber compounds.

2. After a rubber sample has been extracted with acetone it was found: (*a*) That chloroform in every case extracted slightly more material than carbon bisulphide; and (*b*) that constant boiling mixtures, such as 55 per cent carbon bisulphide and 45 per cent acetone, and 68 per cent chloroform and 32 per cent acetone, extracted from many cheap compounds considerably more material than either chloroform or carbon bisulphide.

3. The constant boiling mixture of 68 per cent chloroform and 32 per cent acetone exhibits a marked ability to dissolve vulcanized rubber, as contrasted to the mixture of 55 per cent carbon bisulphide and 45 per cent acetone, which exhibits this ability hardly at all.

4. It is recommended that the constant boiling mixture 55 per cent carbon bisulphide and 45 per cent acetone be used in place of acetone and chloroform to extract rubber samples since:

(*a*) It eliminates one extraction with the necessary weighings.

(*b*) Extraction is complete in 8 hours while the acetone and chloroform extractions require a total of 12 hours.

(*c*) The extraction of free sulphur is complete.

(*d*) A rubber analysis in which the mixed solvent is used is more accurate than that in which acetone and chloroform are used separately, because: (1) Little or no rubber is dissolved by this mixture, as compared with chloroform, which will in some cases dissolve considerable quantities; (2) the extraction of cheap rubber compounds is more complete, since the extracts obtained are greater than the sum of the acetone and chloroform extracts.

H. P. Roberts, L. S. Hanicker, assistant chemists, and W. E. Lange, laboratory assistant, Bureau of Standards, rendered efficient assistance in obtaining the data presented in Tables 2 and 3.

WASHINGTON, September 11, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 163

## STRESSES CAUSED BY COLD-ROLLING

BY

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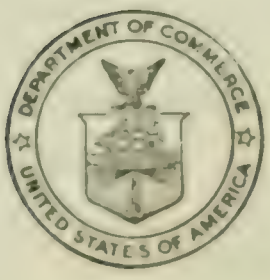
MAY 18 1920

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1920

# STRESSES CAUSED BY COLD-ROLLING

By Henry M. Howe and Edward C. Groesbeck

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Experimental procedure | 3 |
| III. Results | 4 |
| IV. Explanation | 4 |
| 1. Flow of metal due to skin friction | 4 |
| 2. Progressive flattening of the curves of Figs. 3, 4, and 5 | 6 |
| 3. Confirmatory evidence | 7 |
| 4. Extrapolation of results | 7 |
| V. Summary | 7 |
| Appendix.—Details of procedure | 8 |


## I. INTRODUCTION

Prof. A. E. White[1] held that a given total reduction of the thickness of brass condenser tubes was given better by many light drafts than by a few heavy ones, an opinion as to which so competent an observer as W. R. Webster expressed doubt. Later experiments by Mr. Webster[2] were inconclusive.

In studying the effect of variations in the degree of reduction per pass, we should know, among other things, how they affect the intensity of the stresses set up in the metal by the rolling. To that end we have made the experiments here described. As a matter of convenience we operated on strips of soft sheet steel, both because this is a more important material than brass, and because we believe that what is true of one is true qualitatively of the other, and indeed of most metallic masses which resemble them generally in their mechanical properties.

## II. EXPERIMENTAL PROCEDURE

We rolled cold a series of pairs of strips of low-carbon sheet steel as sketched in Figs. 1 and 2, reducing the several strips from their initial thickness of 0.035 to 0.029 inch. We used in some cases 6 heavy reductions or passes, in others 10 passes of intermediate severity, and in still others 31 light passes. We inferred the relative intensity of the residual stresses from the sharpness of the curvature thus induced in the strips, as shown in Fig. 2. Further details of procedure are given in the Appendix.

[1] Proc. Amer. Soc. Test. Mat., 16, Pt. II, p. 151, 1916. [2] Idem, 17, Pt. II, p. 152, 1917.

## III. RESULTS

As shown graphically in Figs. 3, 4, and 5, the spring caused by a given total reduction increases with the amount of reduction per pass. The concordance in these first crude experiments we believe suffices to establish the principle, but more elaborate experiments would be needed to determine the quantitative relations between the effects of light and heavy reductions. In particular, the length of the strips used in the experiments, 3 inches, was too small to enable us to enter them always strictly normally to the vertical plane passing through the axes of the rolls, and

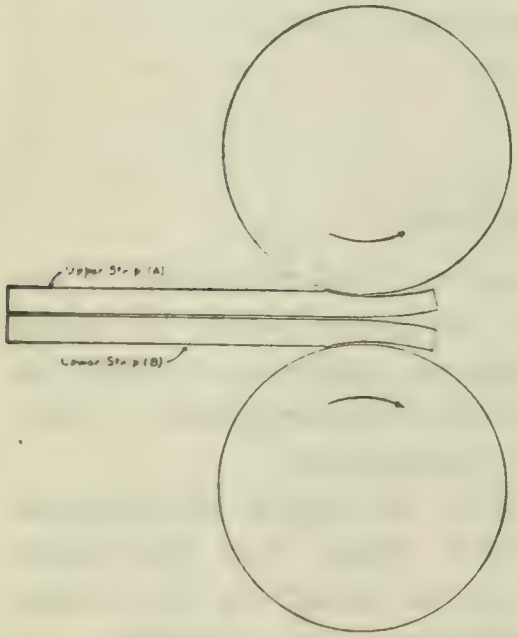


FIG. 1.—*Strips entering the initial pass*

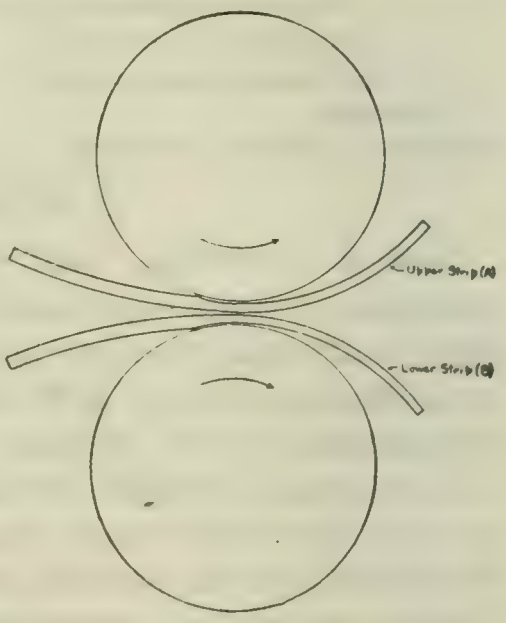


FIG. 2.—*A later pass*

Sketches showing how the spring or arching is caused in two superposed strips by the residual stress induced by cold rolling. The thickness of the strips is exaggerated for clearness of illustration

hence the strips tended to roll diamondwise. This tendency was met by entering them slightly obliquely in the following pass.

## IV. EXPLANATION

### 1. FLOW OF METAL DUE TO SKIN FRICTION

We refer the greater stress caused by the heavier reductions to the greater skin friction produced between the strips and the rolls.

To refresh our memory as to what occurs in rolling, let us suppose that a solid bar *OABDHE*, Fig. 6, enters the rolls so that its face *CG* reaches the plane of their axes, and that its segments *ABC* and *HDG* are squeezed away from the original position by the pressure, with the result that the upper surface of the piece takes the shape *OKC* and the lower surface the shape *ELG*. What becomes of this metal initially in *ABC* and *HDG*? It

flows away from the pressure of the rolls. The vertical component of the flow from each roll is in great part neutralized by the resistance of the other roll, so that most of the flow follows the horizontal component and that the metal flows backwards. For simplicity the slight bulging up and down at $K$ and $L$ may here be ignored.

The friction of the faces of the rolls impedes the backward flow of the metal in immediate contact with them, with the result that the rate of backward flow increases from the upper and lower surfaces of the piece $AB$ and $HD$ toward its axis $PN$. In a solid

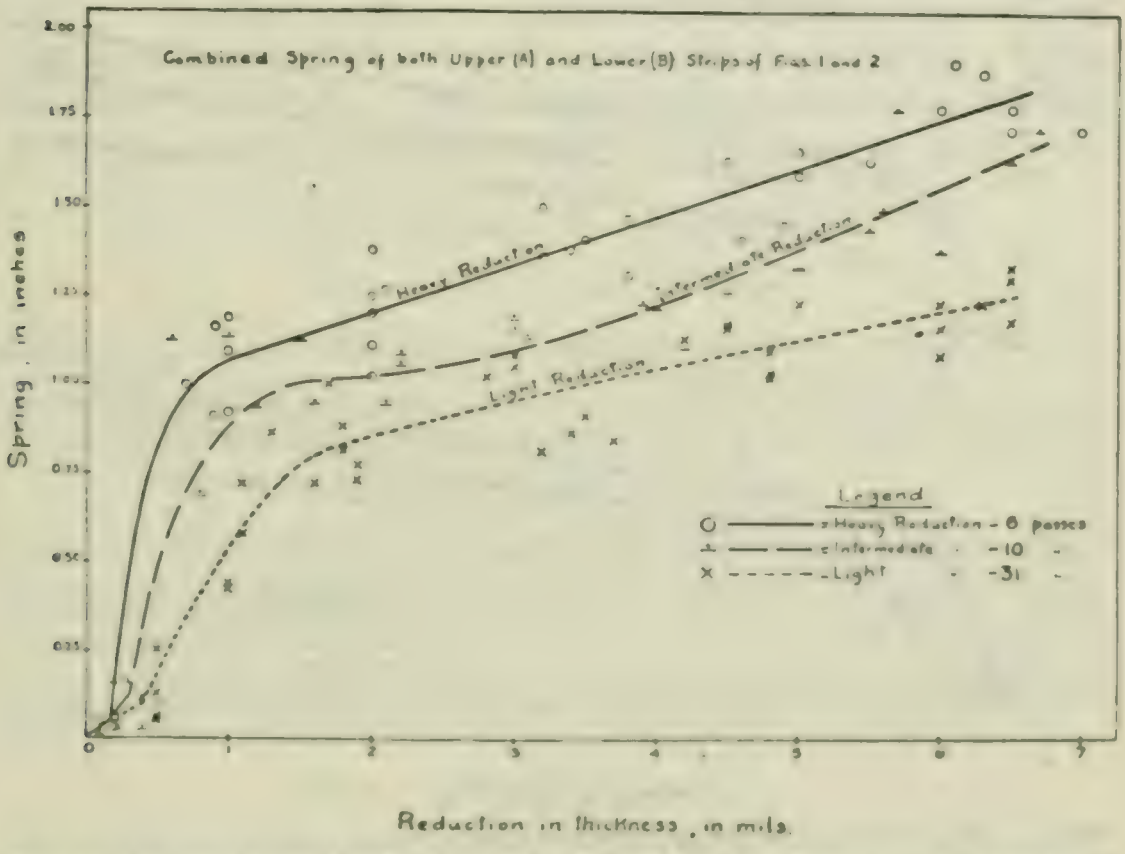
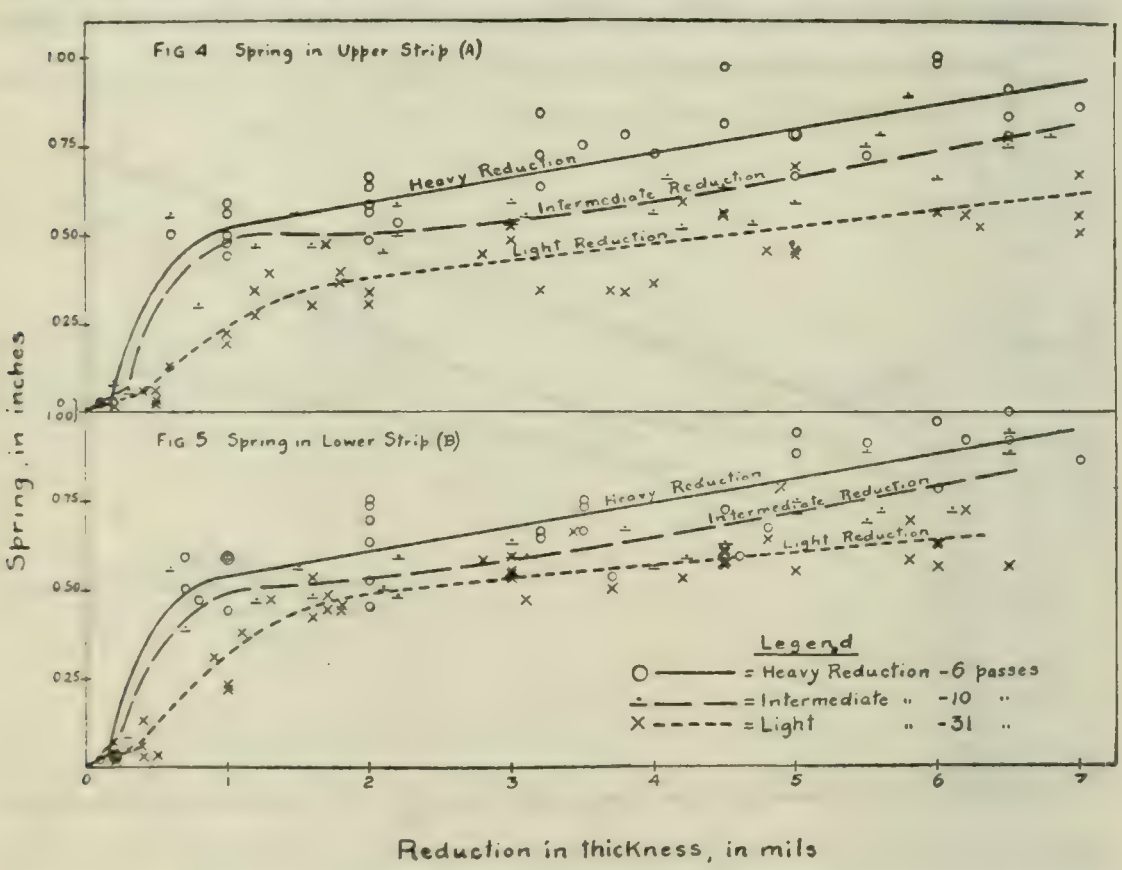

Combined Spring of both Upper (A) and Lower (B) Strips of Pass 1 and 2
Spring, in inches
Heavy Reduction
Intermediate Reduction
Light Reduction
Legend
Heavy Reduction - 6 passes
Intermediate - 10
Light - 31
Reduction in thickness, in mils.

FIG. 3.—*Increase in combined spring produced in both strips of each pair of superposed strips by successive passes.* (*See Fig. 7*)

bar thus rolled cold this progressive difference in the degree of backward flow from surface to axis results in residual stress. But if we suppose that this solid bar $OBDE$ is slit in two along $PN$ so as to give the conditions of our experiments, this same progressive difference causes each of the two strips to bend, so that its face which is next to the roll becomes concave, and that which originally lay along $PN$ becomes convex. The degree of this convexity measures roughly the excess of backward flow along $PN$ over that at the upper and lower faces $OAB$ and $EHD$.

This brings us to our explanation of the phenomenon observed, that for a given total reduction the spring increases with the severity

of reduction in the individual passes, or in other words is approximately inversely as the number of passes used to cause the given reduction. The friction of the face of the rolls is due chiefly to their roughness. Each of the thousands of immeasurably small protuberances on the face of the rolls bites into the metal and impedes its flowing past them, impedes it but does not arrest it, as is proved by the progressive lengthening of even the concave faces of the strips. Clearly the greater the reduction in a given pass, the greater is this frictional impediment to the backward




FIGS. 4 *and* 5.—*Increase in spring produced in the individual strips of each pair of superposed strips by successive passes*

flow at the surface, hence the greater is the ratio of the axial to the surface flow, the greater the internal stress in a solid bar thus rolled, and the greater the convexity induced in a pair of strips as rolled in these experiments.

The explanation thus resides wholly in the increase of the ratio of axial to surface flow caused by increase of surface friction due to increased reduction per pass.

### 2. PROGRESSIVE FLATTENING OF THE CURVES OF FIGS. 3, 4, AND 5

This flattening represents a progressive lessening of the increment of curvature caused in successive passes by the friction of the rolls. A tentative explanation is that, as the strip grows

progressively stiffer because of the plastic deformation, it offers progressively greater resistance to the tendency of the friction of the rolls to increase its curvature.

### 3. CONFIRMATORY EVIDENCE

E. H. Peirce,[3] of the American Steel and Wire Co., finds that a greater total reduction can be endured without rupture in wire drawing with a larger number of light drafts than with a smaller number of heavy ones. Moreover the tensile strength, the ductility as indicated by the various toughness tests, and the elastic limit as indicated by the ability of the wire when in helical springs to endure compression without taking permanent set, are greater for given total reduction when this is caused by a larger number of light drafts. Since internal stress tends to lessen all three of these properties, these observations are in harmony with ours.

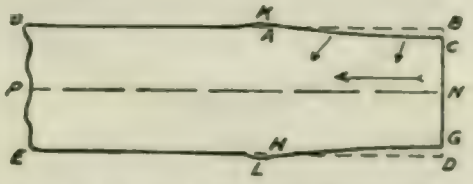


FIG. 6.—*The backward flow of the metal during reduction is greater along the axis than on the surface of the bar and approximately in the directions shown by arrows*

### 4. EXTRAPOLATION OF RESULTS

It may be assumed provisionally that what is true of cold-rolling is true also of drawing through a die, because the action of the rolls approximates that of a rolling die, the grip which draws the metal forward being given by the surface friction of the rolls instead of by a clutch as in wire, spring, and tube drawing.

## V. SUMMARY

1. When the thickness of a pair of strips is reduced by a given amount by cold-rolling, the internal stress, as inferred from the convexity which these strips assume, increases with the amount of reduction per pass. This is ascribed to the skin friction of the rolls.

2. As the rolling progresses the rate of deflection decreases, perhaps because the progressive increase of the stiffness of the strips enables them to resist better the bending effect of the skin friction.

3. The elongation is proportional to the reduction and independent of the number of passes.

[3] Private communication, Mar. 22, 1919.

## APPENDIX.—DETAILS OF PROCEDURE

MATERIAL.—This consisted of common cold-rolled soft sheet steel 0.036 inch in thickness. All the strips were cut from a single sheet. Each of them was 3 inches long and 0.5 inch wide. All were ground to size along the edges, to remove any part that was affected by cutting them from the sheet; they were next annealed at 690–740° C for two hours, and were then ground down to a thickness of 0.035 inch.

THE ROLLS were 2 inches in diameter and 3 inches long.

THE CURVATURE.—The strips were rolled in pairs, one strip being superposed on the other, as in Figs. 1 and 2, and the resultant curvature was determined after each

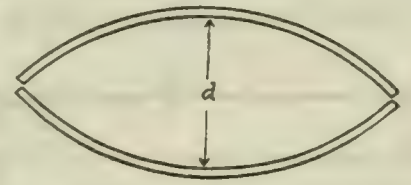



FIG. 7.—*Sketch showing method of measuring the combined spring of the two members of each pair of strips.* (*See Fig. 3*)

pass both by measuring the "rise" or arching of each strip, and also by measuring the total distance between the two members of each pair at their greatest distance apart, *d*, when set together as in Fig. 7.

THE WIDTH of the strips did not change measurably in any case throughout the whole course of the rolling.

THE ELONGATION of the strips as measured along their convex faces was found to be directly proportional to the reduction, and independent of the number of passes by which it was brought about.

THE TOTAL NUMBER OF STRIPS represented by these results was 12 for the heavy, 6 for the intermediate, and 14 for the light reductions.

WASHINGTON, December 4, 1919.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

## No. 164

## SAYBOLT VISCOSITY OF BLENDS

BY

WINSLOW H. HERSCHEL, Associate Physicist

*Bureau of Standards*

JUNE 18, 1920

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# SAYBOLT VISCOSITY OF BLENDS

By Winslow H. Herschel

CONTENTS


| | | Page |
|---|---|---|
| I. | Introduction | 3 |
| II. | Preliminary investigation of the viscosity of mixtures | 4 |
| III. | Blending table | 5 |
| IV. | Graphical methods of interpolation | 10 |
| V. | Comparison with Espy's results | 12 |
| VI. | Tests with gasoline | 14 |
| VII. | Tests with oils from different crudes, but of approximately the same viscosity at the temperature of test | 15 |
| VIII. | Graphical representation of results of tests | 17 |
| IX. | Conclusion | 20 |


## I. INTRODUCTION

Various formulas and diagrams have been published for determining the viscosity of liquid mixtures, but they are mostly expressed in Engler degrees and are not convenient for the user of the Saybolt Universal viscosimeter.[1] Dunstan and Thole[2] quote the Arrhenius formula as modified by Kendall[3]:

$$\log \mu = a \log \mu_1 + b \log \mu_2, \qquad (1)$$

where $a$ and $b$ are the molecular percentage concentrations of the two components in the mixture. They give a table which shows that this formula applies with an error of less than 0.1 per cent to mixtures of carbon tetrachloride and benzene, and conclude:

> These facts militate against the view which recently has been persistently set forth, that fluidity and not viscosity is the essential additive property, and they show that neither fluidity nor viscosity is the true additive property but the logarithms of these quantities (since obviously $\frac{1}{\mu}$ may be substituted for $\mu$ without affecting the result).

Since lubricating oils are not definite chemical compounds, and the values of $a$ and $b$ in equation (1) are unknown, it is necessary

[1] D. Holde, The examination of hydrocarbon oils, translated by E. Mueller, p. 118, 1915. Engler-Höfer, Das Erdöl, 1, p. 60, 1913. F. Schulz, Chem. Rev. 16, p. 401, 1935. H. C. Sherman, T. F. Gray, and H. A. Hammerschlag, Jour. Ind. & Eng. Chem., 1, p. 11, 1909, and T. T. Gray, 8th Int. Cong. Appl. Chem. 10, pp. 161–165, 1913.

[2] A. E. Dunstan and F. B. Thole, the viscosity of liquids, p. 40, 1914.

[3] Meddelanden f. K. Vetensk. Nobelinstitut, 2, p. 23, 1913.

to abandon the probably most accurate form of this equation and revert to the form as originally proposed by Arrhenius [4]:

$$\log \mu = v_1 \log \mu_1 + v_2 \log \mu_2, \tag{2}$$

where $v_1$ and $v_2$ are the percentage volume concentrations, and $\mu_1$ and $\mu_2$ are the viscosities of the two components in the mixture, expressed in cgs units or poises. For a 50 per cent mixture, this equation may be written:

$$\mu = \sqrt{\mu_1 \mu_2}, \tag{3}$$

which is convenient for slide-rule calculations.

## II. PRELIMINARY INVESTIGATION OF THE VISCOSITY OF MIXTURES

Table 1 was calculated from experimental data obtained in previous work,[5] using mixtures of kerosene and spindle oil at 30° C (86° F).

**TABLE 1.—Viscosities of Mixtures of Kerosene and Spindle Oil at 30° C**

| Per cent spindle oil content | Time Engler | Density g/cc | Viscosity in poises [a] | Viscosities calculated on the assumption that the additive property is— | | |
|---|---|---|---|---|---|---|
| | | | | Viscosity | Fluidity | Log viscosity |
| 0 | 55.1 | 0.80 | 0.0117 | ..... | ..... | ..... |
| 25 | 59.8 | .81 | .0206 | 0.0232 | 0.0149 | 0.0202 |
| 50 | 66.7 | .83 | .0348 | .0412 | .0308 | .0357 |
| 75 | 81.3 | .84 | .0618 | .0730 | .0530 | .0622 |
| 100 | 111.8 | .85 | .1113 | ..... | ..... | ..... |

[a] See Winslow H. Herschel, B. S. Tech. Paper No. 125, p. 13, 1919. The first value is calculated by equation (15) and the others by equation (14).

From Table 1, and from other evidence which will be given later, it is believed that equation (2) is the best available as a first approximation for finding the viscosity of mixtures of petroleum oils, or of other liquids which are chemically inert with respect to each other and do not have a definite chemical composition. The errors are, however, very large in some cases, which is to be expected, especially since Dunstan and Thole state that the equation holds fairly well for mixtures of liquids when one component is present to the extent of 90 per cent or more, but it is not valid throughout the whole range of mixtures.

[4] S. Arrhenius, Zeit. Physikal. Chem., 1, p. 285, 1887.

[5] These data were used in preparing Fig. 7, p. 37, of B. S. Tech. Paper No. 100, but have not been published otherwise.

## III. BLENDING TABLE

When the Saybolt Universal viscosimeter is used, the viscosity $\mu$ in poises may be calculated from the Saybolt viscosity, or time of flow in seconds, $t$, by the equation

$$\text{kinematic viscosity} = \frac{\mu}{\gamma} = 0.00220\, t - \frac{1.80}{t} \qquad (4)$$

where $\gamma$ is the density of the oil in grams per cubic centimeter.[6] For very high viscosities equation (4) may be reduced to

$$\text{kinematic viscosity} = 0.00220\, t, \qquad (5)$$

which may be used when the error does not exceed an allowable amount as shown by Table 2.

**TABLE 2.—Error Due to Neglect of Kinetic Energy Correction**

| Saybolt viscosity | Kinematic viscosity by— | | Error in equation 5 |
|---|---|---|---|
| | Equation 4 | Equation 5 | |
| | | | Per cent |
| 32 | 0.0141 | 0.0704 | 400.0 |
| 50 | .0740 | .1100 | 48.7 |
| 75 | .1410 | .1650 | 17.0 |
| 100 | .2020 | .2200 | 8.9 |
| 200 | .4310 | .4400 | 2.1 |
| 300 | .654 | .660 | .9 |
| 400 | .875 | .880 | .5 |
| 500 | 1.096 | 1.100 | .4 |
| 1000 | 2.198 | 2.200 | .1 |

Table 2 shows that the error due to the use of equation (5) will be within the experimental error if the Saybolt viscosity exceeds, say, 300 seconds.

It is common practice for oil refiners or jobbers to carry a relatively small number of oils of different viscosities in stock, and to obtain oils of intermediate viscosities by mixing. Such mixed oils are known as blends.[7]

To avoid at least part of the waste of time and labor involved in cut and try methods, it is desirable that a simple table or diagram, as accurate as possible, should be available to solve the problem of obtaining a blend of definite viscosity from two oils of

[6] Winslow H. Herschel, B. S. Tech. Paper No. [illegible], p. [illegible], [illegible].

[7] It appears from L. Archbutt and R. M. Deeley (Lubrication and lubricants, p. [illegible], 1912) that in England a mixture of petroleum oil with an animal or vegetable oil is known as a blend. In the United States, however, such a mixture would be called a compounded oil. Since the components of a compounded oil are less apt to be chemically inert with respect to each other than are the components of a blend, there would be a probability of greater error in calculating the viscosity of a compounded than of a blended oil. According to Espy: "A certain amount of fatty oil will have a greater effect in raising or lowering the viscosity of a mixture with mineral oil than the same amount of mineral." (W. B. Espy, Petroleum 8, p. [illegible], 1913.)

known viscosity. Since there is no definite relation between the viscosity and the density of oils (except when they are all from the same crude), it is necessary to assume for the sake of simplicity that $\gamma$ is the same for the two components of a blend. Then values of the kinematic viscosity obtained from equation (4) may be used in equation (3) in place of $\mu$ without affecting its validity, and the resulting values of the kinematic viscosity of the blend may be converted into corresponding values of the Saybolt viscosity by means of the equation:

$$t = 227.3\frac{\mu}{\gamma}\left(1 + \sqrt{1 + \frac{0.01584}{\left(\frac{\mu}{\gamma}\right)^2}}\right); \tag{6}$$

or for high viscosities

$$t = 445\frac{\mu}{\gamma}. \tag{7}$$

Table 3 shows the Saybolt viscosities of blends containing 25, 50, and 75 per cent of either of two oils. It was calculated from equations (3) and (4), the need of equation (6) being avoided by using a diagram with Saybolt viscosities plotted against kinematic viscosities.[8] Each line of the table shows values of Saybolt viscosity for blends with a given viscosity of the lighter oil, the headings of the columns showing the viscosity of the heavier oil. Each rectangle formed by the intersection of a line and a column contains three values, which are the viscosities of blends of the two oils in question. Beginning at the top of a rectangle, these values are for blends containing 25, 50, and 75 per cent, respectively, of the heavier oil.

When equations (5) and (7) may be used, it is simple to make corrections for differences in density. If it is assumed that Table 3 applies to unit density, and $\gamma$ is the actual density of a component, the table should be entered with the corrected Saybolt viscosity, which is equal to $t\gamma$. Correcting the viscosities of both components in this manner, and finding from the table (or a similar table for higher viscosities), the uncorrected viscosity of the blend, $T$, it is necessary first to find the density of the blend $\rho$ by taking the weighted arithmetical mean of the densities of the components. Then the desired viscosity of the blend is equal to $\frac{T}{\rho}$.

[8] Data for this diagram may be found in Table 9, p. 21, of B. S. Tech. Paper No. 112, previously referred to.

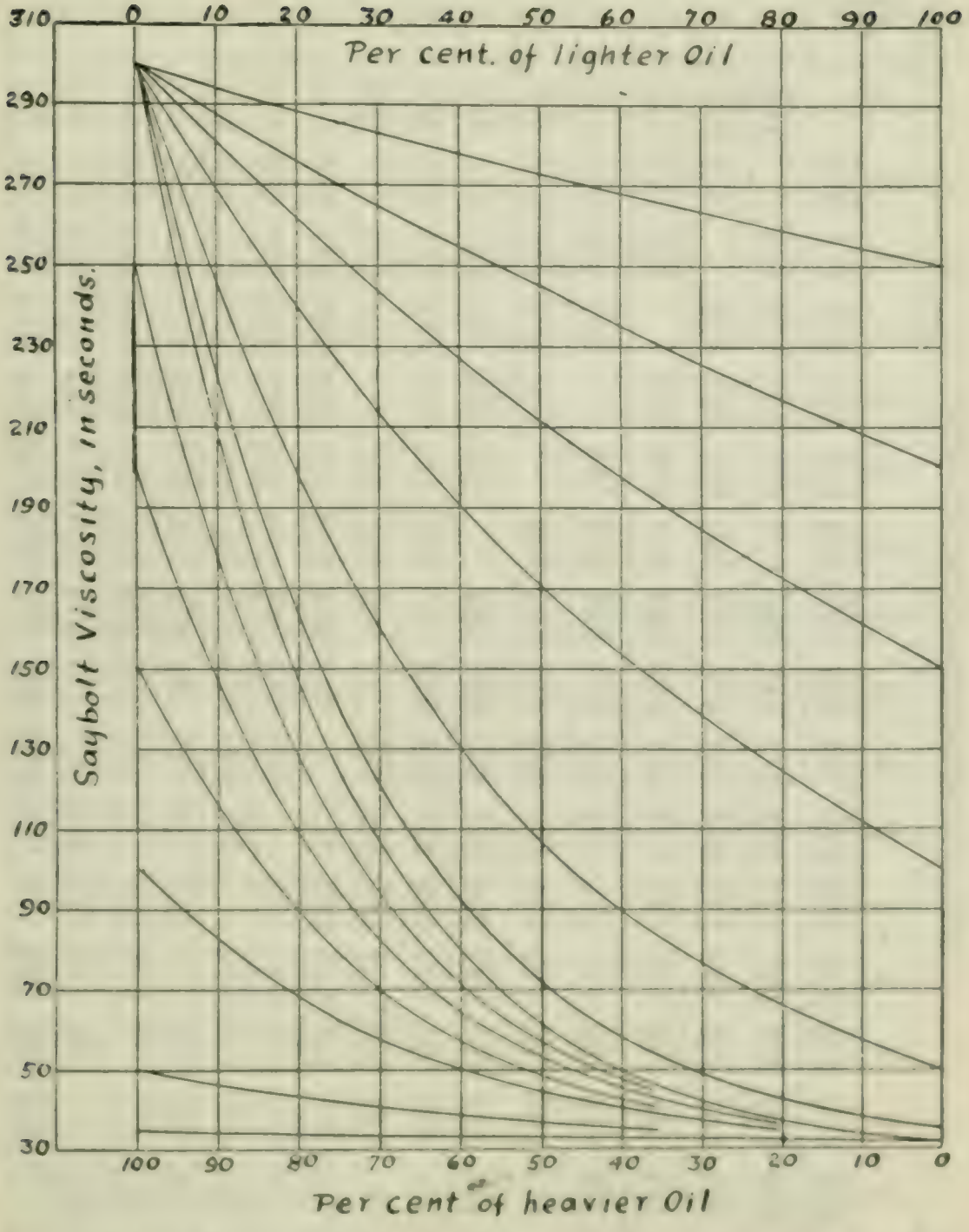


FIG. 1.—*Calculated variations in viscosity of blends with the viscosity and per cent of oils*

**TABLE 3.—Saybolt Viscosities of Blends**

[Both constituents being at the

| Viscosity of heavier oil | | 35 | 40 | 45 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 | 130 | 140 | 150 | 160 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 33 | 33 | 34 | 34 | 35 | 35 | 35 | 36 | 36 | 36 | 36 | 37 | 37 | 37 | 37 |
| | | 33 | 35 | 36 | 37 | 39 | 40 | 41 | 43 | 44 | 45 | 46 | 47 | 47 | 48 | 49 |
| | | 34 | 37 | 40 | 42 | 46 | 50 | 54 | 58 | 62 | 65 | 68 | 72 | 75 | 78 | 81 |
| 300 | 322 | | 36 | 37 | 37 | 38 | 39 | 39 | 40 | 40 | 40 | 41 | 41 | 41 | 42 | 42 |
| | 347 | | 37 | 39 | 40 | 42 | 44 | 46 | 48 | 49 | 51 | 52 | 54 | 55 | 56 | 57 |
| | 372 | | 38 | 42 | 44 | 49 | 54 | 58 | 63 | 67 | 71 | 75 | 79 | 83 | 87 | 91 |
| 290 | 314 | 293 | | 41 | 42 | 42 | 44 | 45 | 45 | 46 | 47 | 47 | 48 | 48 | 48 | 49 |
| | 341 | 295 | | 42 | 44 | 47 | 49 | 52 | 55 | 57 | 59 | 60 | 62 | 63 | 65 | 67 |
| | 369 | 297 | | 43 | 47 | 52 | 58 | 63 | 68 | 73 | 78 | 82 | 87 | 91 | 95 | 100 |
| 280 | 305 | 285 | 282 | | 46 | 48 | 49 | 50 | 52 | 52 | 53 | 54 | 55 | 56 | 57 | 57 |
| | 334 | 290 | 285 | | 47 | 52 | 55 | 58 | 61 | 63 | 65 | 67 | 69 | 71 | 73 | 75 |
| | 366 | 294 | 287 | | 49 | 56 | 61 | 67 | 73 | 78 | 83 | 88 | 93 | 98 | 102 | 107 |
| 270 | 297 | 277 | 274 | 272 | | 52 | 54 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 |
| | 328 | 283 | 279 | 275 | | 55 | 59 | 62 | 65 | 68 | 71 | 73 | 76 | 78 | 80 | 82 |
| | 362 | 290 | 284 | 277 | | 57 | 64 | 70 | 76 | 82 | 87 | 92 | 98 | 103 | 108 | 113 |
| 260 | 289 | 272 | 269 | 266 | 263 | | 62 | 63 | 65 | 66 | 68 | 69 | 70 | 71 | 72 | 73 |
| | 322 | 279 | 274 | 270 | 265 | | 64 | 68 | 72 | 76 | 79 | 81 | 84 | 87 | 90 | 93 |
| | 359 | 289 | 282 | 275 | 267 | | 67 | 74 | 80 | 87 | 93 | 99 | 105 | 110 | 115 | 120 |
| 250 | 280 | 261 | 259 | 257 | 255 | 252 | | 72 | 74 | 75 | 77 | 78 | 80 | 81 | 82 | 83 |
| | 316 | 273 | 269 | 264 | 260 | 255 | | 74 | 79 | 83 | 86 | 89 | 93 | 95 | 99 | 102 |
| | 355 | 285 | 278 | 271 | 264 | 257 | | 77 | 84 | 91 | 98 | 102 | 109 | 115 | 121 | 127 |
| 240 | 272 | 253 | 251 | 249 | 247 | 244 | 242 | | 82 | 84 | 86 | 87 | 89 | 91 | 92 | 94 |
| | 309 | 268 | 263 | 259 | 254 | 250 | 245 | | 85 | 89 | 93 | 96 | 101 | 104 | 108 | 111 |
| | 352 | 283 | 276 | 269 | 262 | 255 | 247 | | 87 | 95 | 101 | 106 | 115 | 120 | 126 | 133 |
| 230 | 264 | 245 | 243 | 241 | 239 | 237 | 235 | 233 | | 93 | 95 | 96 | 98 | 100 | 101 | 103 |
| | 302 | 263 | 259 | 254 | 250 | 245 | 240 | 235 | | 95 | 100 | 103 | 107 | 111 | 115 | 119 |
| | 348 | 280 | 273 | 266 | 259 | 252 | 245 | 238 | | 97 | 105 | 111 | 118 | 124 | 132 | 139 |
| 220 | 255 | 237 | 236 | 234 | 232 | 229 | 227 | 225 | 222 | | 103 | 105 | 107 | 109 | 110 | 112 |
| | 296 | 257 | 252 | 248 | 244 | 239 | 235 | 230 | 225 | | 104 | 109 | 114 | 118 | 122 | 126 |
| | 344 | 276 | 270 | 262 | 256 | 249 | 242 | 235 | 227 | | 108 | 115 | 122 | 129 | 135 | 142 |
| 210 | 246 | 229 | 227 | 225 | 224 | 221 | 219 | 217 | 215 | 212 | | 112 | 114 | 116 | 118 | 120 |
| | 289 | 251 | 247 | 243 | 239 | 234 | 229 | 225 | 220 | 215 | | 114 | 119 | 124 | 128 | 132 |
| | 340 | 274 | 267 | 260 | 253 | 246 | 239 | 232 | 225 | 217 | | 117 | 124 | 131 | 138 | 145 |
| 200 | 237 | 221 | 219 | 218 | 216 | 214 | 211 | 209 | 207 | 205 | 202 | | 121 | 124 | 126 | 129 |
| | 282 | 245 | 241 | 237 | 233 | 228 | 224 | 219 | 215 | 210 | 205 | | 124 | 129 | 134 | 138 |
| | 335 | 270 | 263 | 257 | 250 | 243 | 236 | 229 | 222 | 215 | 207 | | 128 | 135 | 142 | 149 |
| 190 | 228 | 213 | 211 | 209 | 208 | 206 | 204 | 201 | 199 | 197 | 195 | 192 | | 132 | 134 | 136 |
| | 274 | 238 | 234 | 230 | 226 | 222 | 218 | 213 | 208 | 204 | 199 | 195 | | 135 | 139 | 143 |
| | 331 | 266 | 260 | 253 | 246 | 240 | 233 | 226 | 219 | 212 | 205 | 197 | | 138 | 145 | 152 |
| 180 | 219 | 204 | 202 | 200 | 199 | 197 | 195 | 193 | 191 | 189 | 187 | 185 | 182 | | 142 | 145 |
| | 267 | 231 | 228 | 224 | 220 | 216 | 212 | 208 | 203 | 199 | 194 | 190 | 185 | | 144 | 149 |
| | 326 | 263 | 257 | 250 | 244 | 237 | 230 | 223 | 216 | 208 | 201 | 194 | 187 | | 147 | 154 |
| 170 | 210 | 195 | 194 | 192 | 190 | 189 | 187 | 185 | 183 | 181 | 179 | 177 | 175 | 172 | | 152 |
| | 259 | 225 | 222 | 218 | 214 | 210 | 206 | 202 | 198 | 193 | 189 | 184 | 180 | 175 | | 155 |
| | 321 | 260 | 254 | 247 | 241 | 234 | 227 | 220 | 213 | 206 | 199 | 192 | 185 | 177 | | 157 |
| 160 | 200 | 187 | 186 | 184 | 183 | 181 | 179 | 177 | 175 | 174 | 172 | 170 | 167 | 165 | 163 | |
| | 252 | 218 | 215 | 211 | 208 | 204 | 200 | 196 | 192 | 188 | 183 | 179 | 174 | 170 | 165 | |
| | 316 | 256 | 250 | 244 | 237 | 231 | 224 | 217 | 210 | 204 | 197 | 190 | 183 | 175 | 168 | |
| | 400 | 300 | 290 | 280 | 270 | 260 | 250 | 240 | 230 | 220 | 210 | 200 | 190 | 180 | 170 | |

VISCOSITIES OF LIGHTER OIL OVER 160 VISCOSITY

VISCOSITIES OF HEAVIER OIL, FOR LIGHTER OILS OVER 160 VISCOSITY

NOTE.—The three values in each group are vicosities of blends of the three percentage compositions given above.

**Containing 25, 50, and 75 Per Cent of Heavier Oil**

same temperature as the blend.]

| 170 | 180 | 190 | 200 | 210 | 220 | 230 | 240 | 250 | 260 | 270 | 280 | 290 | 300 | 400 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 37 | 37 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 39 | 39 | 39 | 39 | 39 | 40 | |
| 50 | 51 | 52 | 53 | 53 | 54 | 55 | 56 | 57 | 57 | 58 | 59 | 60 | 61 | 65 | 32 |
| 84 | 88 | 91 | 93 | 96 | 99 | 103 | 106 | 109 | 112 | 114 | 117 | 120 | 123 | 150 | |
| 42 | 43 | 43 | 43 | 43 | 43 | 43 | 43 | 44 | 44 | 44 | 44 | 44 | 45 | 46 | |
| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 79 | 35 |
| 94 | 98 | 101 | 105 | 108 | 111 | 115 | 118 | 122 | 125 | 128 | 131 | 135 | 138 | 170 | |
| 50 | 50 | 50 | 51 | 51 | 51 | 51 | 52 | 52 | 52 | 53 | 53 | 53 | 54 | 55 | |
| 69 | 70 | 72 | 73 | 74 | 75 | 77 | 78 | 79 | 80 | 81 | 83 | 84 | 85 | 96 | 40 |
| 105 | 109 | 113 | 117 | 121 | 125 | 129 | 133 | 137 | 140 | 144 | 148 | 152 | 155 | 191 | |
| 58 | 58 | 59 | 59 | 60 | 60 | 60 | 61 | 61 | 62 | 62 | 63 | 63 | 64 | 66 | |
| 77 | 79 | 81 | 83 | 85 | 86 | 88 | 90 | 91 | 93 | 94 | 96 | 97 | 99 | 112 | 45 |
| 112 | 118 | 122 | 126 | 130 | 135 | 139 | 143 | 148 | 152 | 156 | 160 | 165 | 169 | 208 | |
| 64 | 65 | 65 | 66 | 66 | 67 | 67 | 68 | 68 | 69 | 69 | 70 | 70 | 71 | 74 | |
| 85 | 87 | 89 | 91 | 93 | 95 | 97 | 99 | 100 | 102 | 104 | 105 | 107 | 108 | 124 | 50 |
| 118 | 124 | 128 | 132 | 137 | 142 | 147 | 151 | 155 | 160 | 164 | 168 | 173 | 177 | 220 | |
| 74 | 75 | 75 | 76 | 77 | 77 | 78 | 79 | 80 | 80 | 81 | 81 | 82 | 82 | 87 | |
| 96 | 98 | 100 | 102 | 104 | 106 | 108 | 110 | 113 | 115 | 117 | 119 | 121 | 123 | 141 | 60 |
| 126 | 131 | 136 | 142 | 147 | 152 | 157 | 162 | 166 | 171 | 176 | 181 | 186 | 191 | 235 | |
| 84 | 85 | 86 | 88 | 89 | 90 | 91 | 92 | 92 | 93 | 94 | 94 | 95 | 96 | 102 | |
| 105 | 108 | 111 | 113 | 116 | 119 | 121 | 124 | 126 | 129 | 131 | 133 | 135 | 138 | 157 | 70 |
| 133 | 139 | 144 | 150 | 155 | 160 | 165 | 170 | 176 | 182 | 187 | 192 | 198 | 202 | 249 | |
| 95 | 97 | 98 | 99 | 100 | 101 | 102 | 102 | 103 | 104 | 105 | 106 | 106 | 107 | 115 | |
| 114 | 118 | 121 | 124 | 126 | 129 | 132 | 135 | 138 | 140 | 143 | 145 | 148 | 150 | 171 | 80 |
| 139 | 144 | 150 | 156 | 162 | 168 | 173 | 179 | 185 | 190 | 196 | 201 | 206 | 212 | 260 | |
| 105 | 106 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 128 | |
| 122 | 126 | 129 | 132 | 135 | 139 | 141 | 144 | 147 | 149 | 152 | 155 | 157 | 160 | 184 | 90 |
| 145 | 150 | 156 | 162 | 168 | 174 | 180 | 186 | 192 | 197 | 202 | 208 | 213 | 219 | 271 | |
| 114 | 115 | 117 | 118 | 120 | 121 | 122 | 123 | 125 | 126 | 127 | 128 | 129 | 131 | 139 | |
| 130 | 133 | 137 | 140 | 143 | 146 | 150 | 153 | 156 | 159 | 162 | 165 | 168 | 171 | 196 | 100 |
| 148 | 155 | 161 | 168 | 174 | 180 | 186 | 192 | 198 | 204 | 209 | 215 | 220 | 226 | 279 | |
| 122 | 124 | 125 | 127 | 129 | 130 | 131 | 133 | 134 | 135 | 137 | 138 | 139 | 140 | 149 | |
| 136 | 140 | 143 | 147 | 150 | 153 | 157 | 160 | 164 | 167 | 170 | 173 | 177 | 180 | 206 | 110 |
| 151 | 158 | 165 | 171 | 178 | 184 | 190 | 196 | 202 | 208 | 214 | 220 | 226 | 232 | 287 | |
| 131 | 133 | 135 | 136 | 138 | 140 | 141 | 142 | 144 | 145 | 146 | 147 | 148 | 149 | 160 | |
| 142 | 146 | 150 | 153 | 157 | 160 | 164 | 168 | 171 | 175 | 178 | 182 | 185 | 188 | 215 | 120 |
| 156 | 162 | 169 | 176 | 182 | 188 | 195 | 201 | 207 | 213 | 219 | 225 | 231 | 237 | 293 | |
| 138 | 140 | 142 | 144 | 145 | 147 | 148 | 150 | 151 | 153 | 154 | 156 | 157 | 158 | 170 | |
| 147 | 152 | 156 | 160 | 164 | 168 | 172 | 176 | 179 | 183 | 186 | 190 | 193 | 196 | 225 | 130 |
| 159 | 165 | 172 | 179 | 185 | 192 | 199 | 205 | 211 | 218 | 224 | 230 | 236 | 242 | 300 | |
| 147 | 149 | 150 | 152 | 154 | 155 | 157 | 158 | 160 | 161 | 163 | 164 | 166 | 167 | 180 | |
| 154 | 158 | 162 | 167 | 171 | 175 | 179 | 182 | 186 | 190 | 194 | 197 | 200 | 204 | 234 | 140 |
| 161 | 166 | 175 | 182 | 189 | 195 | 202 | 209 | 215 | 222 | 228 | 234 | 241 | 247 | 306 | |
| 155 | 157 | 159 | 161 | 163 | 165 | 167 | 168 | 170 | 172 | 173 | 175 | 176 | 178 | 190 | |
| 159 | 164 | 169 | 173 | 178 | 182 | 186 | 190 | 193 | 197 | 200 | 204 | 207 | 211 | 244 | 150 |
| 165 | 172 | 179 | 186 | 193 | 200 | 207 | 213 | 220 | 226 | 232 | 239 | 245 | 252 | 311 | |
| 163 | 165 | 167 | 170 | 172 | 174 | 175 | 177 | 179 | 181 | 183 | 184 | 186 | 187 | 200 | |
| 165 | 170 | 174 | 179 | 183 | 188 | 192 | 196 | 200 | 204 | 208 | 211 | 215 | 218 | 252 | 160 |
| 168 | 175 | 183 | 190 | 197 | 204 | 210 | 217 | 224 | 231 | 237 | 244 | 250 | 256 | 316 | |
| 170 | 180 | 190 | 200 | 210 | 220 | 230 | 240 | 250 | 260 | 270 | 280 | 290 | 300 | 400 | |

VISCOSITIES OF LIGHTER OIL LESS THAN 160 VISCOSITY

VISCOSITIES OF HEAVIER OIL, FOR LIGHTER OILS LESS THAN 160 VISCOSITY

It seems probable that an extension of Table 3 to higher viscosities might prove serviceable in estimating the viscosity of oils too viscous to be run in the Saybolt viscosimeter. The viscosity of the lighter component and of the blend could be determined by viscosimeter, and then the viscosity of the more viscous component found from the table.

## IV. GRAPHICAL METHODS OF INTERPOLATION

On account of the large number of variables involved, it is difficult to represent Table 3 graphically. Any pair of oils may be selected, as in Fig. 1, but to give all the information in the table in this manner would necessitate a large number of diagrams with

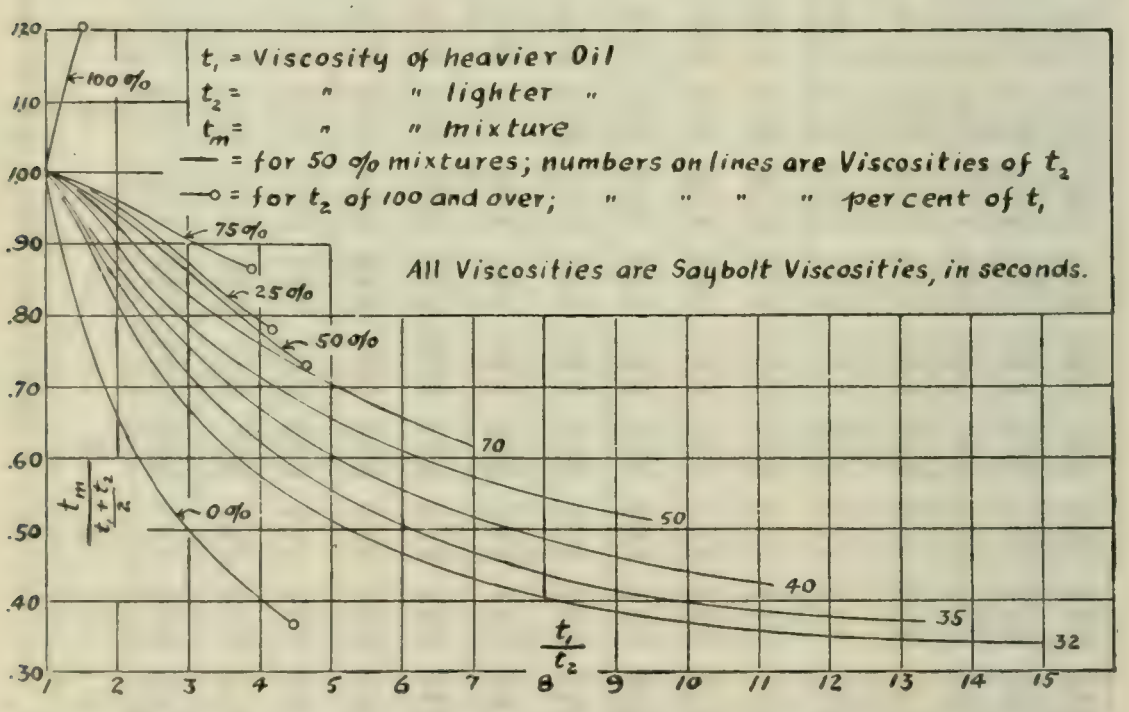


FIG. 2.—*Relation between calculated viscosities of blends, when the additive property is assumed to be the Saybolt viscosity and when it is assumed to be the logarithm of the viscosity in poises*

no ready means of interpolating between them. It will be noted that the greater the difference in the viscosity of the component oils, the greater the curvature of the lines, which would be straight if Saybolt viscosities were additive. In reality two errors are involved in the assumption that Saybolt viscosities are additive, since they are not proportional to viscosities in poises, and even the latter are not additive.

Lockhart [9] says that when there is a considerable difference in viscosity of the component oils the viscosity of a blend may be as much as 30 per cent below the viscosity calculated from the vis-

[9] L. B. Lockhart, American lubricants, p. 18; 1918.

cosity of the two oils and the proportions taken; that is, calculated on the erroneous assumption above referred to. As will be seen, the error may be much greater than 30 per cent.

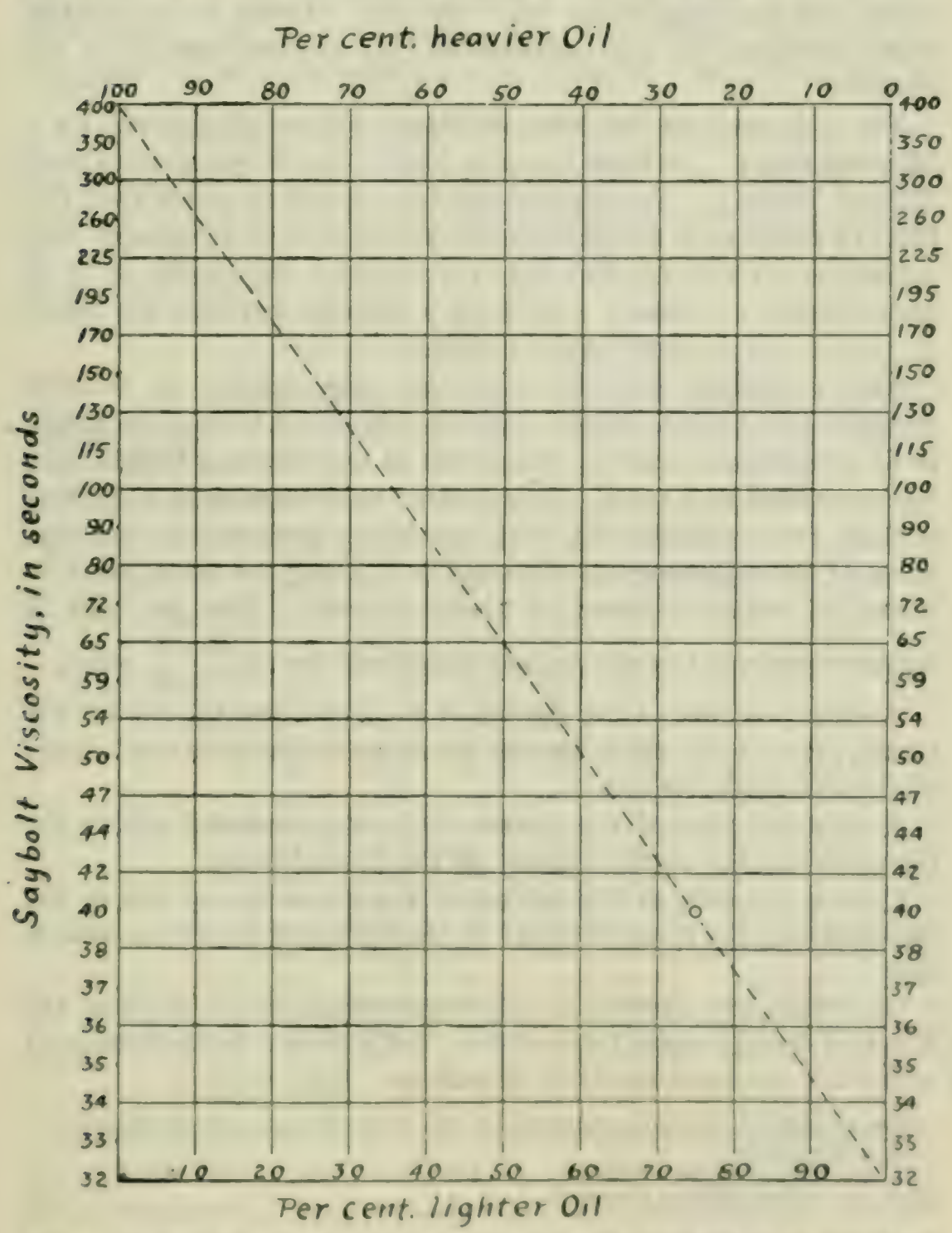


FIG. 3.—*Diagram for interpolating the viscosity of a blend, calculated on the assumption that the additive property is the logarithm of the viscosity in force.*

In order to reduce the number of variables, and be able to present more information on one diagram, Fig. 2 was calculated from the data of Table 3. While it gives no data for the lighter oils, except for 50 per cent blends, it might serve to estimate viscosities

of blends containing not less than 25 per cent of either oil, when both oils had a viscosity of at least 100 seconds. The figure shows that in the extreme case of mixing oils of 32 and 300 seconds viscosity, the resulting blend has a viscosity of only 37 per cent of that calculated on the assumption that Saybolt viscosities are additive.

Fig. 3 is perhaps the most satisfactory form of diagram for a blending chart. Its form is due to Espy,[10] but it was plotted from data of Table 3. No attempt has been made to prove that this form of diagram is mathematically exact, and in agreement with equations (2) and (4), but Fig. 3 was found graphically to be in approximate agreement with Espy's diagram between the limits of 55 and 300 seconds, Saybolt viscosity.

Espy's method may be expressed algebraically as follows: Suppose two oils of widely differing viscosities have been mixed in all proportions, and the viscosities of the resulting blends have been recorded in a table. It is desired to determine in what proportion two available oils, with viscosities intermediate between those of the experimental oils used in deriving the table, must be mixed to obtain a blend of given viscosity. The per cent of lighter component in the desired blend will be $100\frac{B-A}{C-A}$, where

$A$ = the per cent of the lighter of the experimental oils in the blend, given in the table, having the same viscosity as the heavier of the two available oils.

$B$ = the per cent of the lighter of the experimental oils in the blend having the same viscosity as the desired blend.

$C$ = the per cent of the lighter of the experimental oils in the blend having the same viscosity as the lighter of the two available oils.

Obviously any method is only approximate which neglects the effect of density upon time of flow, but within a limited range of viscosities the error may not be serious. Espy says:

> The viscosity of a blend, calculated by the above method, will check within a limit of three points;

that is, within three seconds.

## V. COMPARISON WITH ESPY'S RESULTS

In order to check Espy's results more accurately, a series of tests was made with two oils of approximately the same viscosities as used by him. The specific gravities of these oils were 0.850 for the light and 0.878 for the heavy, while Espy's values were

[10] W. E. Espy, Petroleum, 8, p. 27; 1919.

0.872 and 0.903, respectively.[11] If $\mu$ is the viscosity as calculated from equation (4), and $\mu'$ is the viscosity of a blend, in poises, as estimated from the viscosities of the two components, then $\frac{\mu}{\mu'}$, is a correction factor by which viscosities of a blend, estimated by equation (2), must be multiplied to obtain the values as given by test. $\frac{t}{t'}$ is a corresponding correction factor for Saybolt viscosities.

Table 4 shows correction factors calculated from results of tests. In order to avoid the error in the assumption of constant density, no use was made of Table 3, but the table was calculated directly from equations (2), (4), and (5).

**TABLE 4.—Check of Espy's Results**

| Percentage of lighter oil in blend | W. E. Espy tests at 100° F (37.8° C) | | | | Bureau of Standards tests at 68° F (20° C) | | | |
|---|---|---|---|---|---|---|---|---|
| | $t$ | $\mu$ | $\frac{t}{t'}$ | $\frac{\mu}{\mu'}$ | $t$ | $\mu$ | $\frac{t}{t'}$ | $\frac{\mu}{\mu'}$ |
| 100 | 55 | 0.0754 | | | 56.2 | 0.0775 | | |
| 95 | 57 | .0804 | 0.977 | 0.964 | 60.1 | .0866 | 1.005 | 1.012 |
| 90 | 60 | .0876 | .967 | .948 | 63.1 | .0936 | .994 | .991 |
| 85 | 64 | .0968 | .965 | .944 | 66.0 | 1002 | .974 | .961 |
| 80 | 68 | .1060 | .955 | .934 | 70.1 | 1094 | .971 | .951 |
| 75 | 72 | .1153 | .937 | .918 | 74.8 | 1198 | .954 | .940 |
| 70 | 76 | .1240 | .916 | .893 | 80.2 | 1318 | .951 | .937 |
| 65 | 81 | .1351 | .902 | 878 | 85.2 | 1424 | .933 | .919 |
| 60 | 87 | .1483 | 892 | 870 | 90.4 | 1534 | .913 | .897 |
| 55 | 95 | .1653 | .895 | .876 | 98.2 | .1698 | .911 | 898 |
| 50 | 103 | .1823 | 889 | .872 | 107.8 | .1895 | .920 | .909 |
| 45 | 112 | .2014 | 886 | 869 | 114.6 | 2037 | .897 | 884 |
| 40 | 122 | .2220 | .880 | 866 | 124.5 | 2239 | .891 | 881 |
| 35 | 135 | .2486 | .886 | 876 | 141.5 | .2580 | 924 | 921 |
| 30 | 149 | .2776 | 890 | 882 | 154.5 | 2849 | 922 | .917 |
| 25 | 167 | .3139 | 907 | 901 | 169.2 | .3138 | 921 | 917 |
| 20 | 185 | 3502 | 914 | 908 | 187.0 | .3490 | .926 | 923 |
| 15 | 205 | 3900 | .918 | 916 | 203.1 | 3813 | .916 | 915 |
| 10 | 229 | .4390 | 932 | 927 | 240.4 | 4540 | 957 | 945 |
| 5 | 254 | 4895 | 936 | 935 | 267.3 | .507 | 946 | 946 |
| 0 | 300 | 580 | | | 293.2 | 562 | | |

It will be noticed that there is considerable difference between the correction factors for viscosities in poises and in time of flow for a given test. These values approach each other as the viscosity increases or the kinetic energy correction decreases, and they would be equal for very high viscosities for which equations (5) and (7) are valid. Table 4 also shows that there is a systematic error in Table 3 other than that due to the disregard of variations in density in calculations involving equations (4) and (6). Assum-

[11] Private communication.

ing these equations to be correct, there must be a systematic error in equation (2) which requires further investigation.

## VI. TESTS WITH GASOLINE

The Saybolt Universal viscosimeter should not be used for gasolines or other liquids having a viscosity of less than 32 seconds, but if this is done, equations (4) and (6) must be replaced by

$$\frac{\mu}{\gamma}=0.00130\,t-\frac{0.93}{t} \tag{8}$$

and

$$t=385\frac{\mu}{\gamma}\left(1+\sqrt{1+\frac{0.00484}{\left(\frac{\mu}{\gamma}\right)^2}}\right) \tag{9}$$

Under these conditions the flow is turbulent, and the time of discharge is influenced only slightly by a considerable change in $\mu$, the viscosity in poises, as shown by Table 5. In calculating this table no use was made of equation (8), viscosities in poises being obtained by the Ubbelohde viscosimeter,[12] but equation (9) was used to obtain values of $t$ marked with an asterisk (*).

**TABLE 5.—Tests of 50 Per Cent Blends of Oils from Various Crudes with Gasoline and Other Diluents, at 20° C (68° F)**

| Oils | Specific gravity $\frac{15.6°}{15.6°}$C | $t$ | $\mu$ | $\frac{t}{t'}$ | $\frac{\mu}{\mu'}$ | Percentage error in $\mu$ if additive property is— | |
|---|---|---|---|---|---|---|---|
| | | | | | | log $\mu$ | $1/\mu$ |
| 1. Pennsylvania | 0.864 | 259.7 | 0.485 | | | | |
| 2. Mid continent | .901 | 668.6 | 1.315 | | | | |
| 3. Texas | .932 | 673.9 | 1.361 | | | | |
| 4. California | .942 | 390.4 | .788 | | | | |
| 5. Mineral seal | .832 | 54.0 | .0708 | | | | |
| 6. Kerosene | .782 | 33.9 | .0172 | | | | |
| 7. Commercial gasoline | .743 | * 30.0 | .0059 | | | | |
| 8. Aviation gasoline | .700 | * 28.8 | .0036 | | | | |
| 50 per cent blends: | | | | | | | |
| 1+5 | | 95.4 | .1613 | 0.888 | 0.871 | 14.9 | 61.7 |
| 1+6 | | 53.3 | .0694 | .849 | .761 | 31.4 | 76.1 |
| 1+7 | | 38.8 | .0313 | .816 | .584 | 71.6 | 81.2 |
| 1+8 | | 36.0 | .0229 | .840 | .546 | 83.4 | 84.4 |
| 2+5 | | 130.8 | .2360 | .790 | .774 | 30.6 | 71.6 |
| 2+6 | | 59.6 | .0859 | .667 | .572 | 74.9 | 80.3 |
| 2+7 | | 41.2 | .0386 | .665 | .437 | 129.0 | † 84.8 |
| 2+8 | | 39.4 | .0328 | .727 | .475 | 110.7 | † 89.1 |
| 3+5 | | 117.9 | .2131 | .708 | .687 | 45.7 | 68.4 |
| 3+6 | | 56.1 | .0788 | .626 | .516 | 94.0 | † 78.6 |
| 3+7 | | 39.8 | .0353 | .641 | .393 | 154.7 | † 83.4 |
| 3+8 | | 35.4 | .0219 | .648 | .312 | 221.0 | † 83.6 |
| 4+5 | | 104.6 | .1861 | .839 | .788 | 26.9 | 65.1 |
| 4+6 | | 53.1 | .0716 | .734 | .616 | 62.4 | 76.6 |
| 4+7 | | 38.2 | .0308 | .726 | .450 | 122.0 | † 80.9 |
| 4+8 | | 34.7 | .0200 | .736 | .374 | 167.5 | † 82.0 |

[12] Winslow H. Herschel, B. S. Tech. Paper No. 125; 1919.

A table similar to Table 3, but extended to still lower viscosities might perhaps be used to gain a rough idea of the viscosity of a gasoline. The viscosity of a blend and of the component heavy oil could be determined by instrument, and the viscosity of the component gasoline could then be taken from the table. But this and all other uses, in open viscosimeters, of blends containing gasoline is subject to large errors on account of the evaporation of the gasoline from the blend.

The tests of Tables 4 and 5 show that the assumption that the additive property is log $\mu$ does not give as low a viscosity of blend as found by test, and, as shown in Table 1, the only other common assumption which would enable a lower viscosity to be predicted is that fluidities are additive. This indicated that this latter assumption might give better results in extreme cases. As shown in the last column of Table 5, this is the case in tests marked with a dagger (†), but the errors are so great with either assumption that there is not much choice between them.

Table 5 shows that the error in calculating the viscosity of a 50 per cent blend varies greatly, but it does not show clearly how much of this variation is due to the source of the oils and how much to the difference in range of viscosity between the two components of a blend. According to Espy the variation due to differences in crudes is negligible, although, as will be seen, this conclusion is probably due to the limited range of his experiments.

## VII. TESTS WITH OILS FROM DIFFERENT CRUDES, BUT OF APPROXIMATELY THE SAME VISCOSITY AT THE TEMPERATURE OF TEST

Two heavy oils, N and P, one of naphthene and the other of paraffin crude, of approximately the same viscosity at 55° C (131° F), were selected and blended with two lighter oils, M and Q, of the same crudes. It was desired to use heavier oils than in the tests with gasoline, and this necessitated an increase in temperature. With a time of flow much over 500 seconds, it is very difficult to get check results, but, on the other hand, if the time is decreased by an increase of temperature, there is an increase in the error due to the change of volume of the oil after it leaves the outlet tube. The temperature of 55° C was adopted as a compromise between these considerations.

By making the four possible 50 per cent blends of oils of different viscosities it was found that the maximum correction factor was obtained for a blend of N and Q and a minimum factor

for a blend of P and M. It is noteworthy that these last two blends are both of unlike crudes. The assumption seemed reasonable that the maximum and minimum correction factors for blends of any proportion would follow the same law, and the tests of Table 6 appear to confirm this.

Table 6 shows that the correction factor is lower when the heavy oil is of naphthene than of paraffin base. In order to see whether this rule was still valid when kerosenes of the two crudes were used as diluents, the final series of tests were run with the results as shown in Table 7. The Saybolt viscosities marked with an asterisk (and also that of the kerosene in Table 5) were calculated from the viscosity as determined by the Ubbelohde viscosimeter. The letters in Table 7 have the same significance as regards the source of the oils as in Table 6, but the viscosities of the oils are different in the two tables.

TABLE 6.—Tests of Blends of Unlike Crudes at 55° C (131° F)

| Oils | Percentage of lighter oil in blend | Specific gravity $\frac{15.6°}{15.6°C}$ | $t$ | $\mu$ | $\frac{t}{t'}$ | $\frac{\mu}{\mu'}$ |
|---|---|---|---|---|---|---|
| N+Q | 100 | 0.885 | 111.5 | 0.1965 | ..... | ..... |
| | 90 | ..... | 122.7 | .2202 | 0.945 | 0.940 |
| | 80 | ..... | 134.0 | .2441 | .883 | .874 |
| | 70 | ..... | 152.1 | .2817 | .853 | .845 |
| | 60 | ..... | 181.1 | .3410 | .863 | .857 |
| | 50 | ..... | 209.7 | .3990 | .846 | .842 |
| | 30 | ..... | 290.2 | .565 | .839 | .837 |
| | 20 | ..... | 343.6 | .674 | .847 | .837 |
| | 10 | ..... | 424.0 | .838 | .873 | .877 |
| | 0 | .934 | 577.4 | 1.147 | ..... | ..... |
| P–M | 100 | .925 | 111.7 | .2060 | ..... | ..... |
| | 90 | ..... | 126.6 | .2363 | .977 | .975 |
| | 85 | ..... | 136.3 | .2557 | .972 | .971 |
| | 80 | ..... | 144.2 | .2710 | .952 | .949 |
| | 70 | ..... | 170.2 | .3220 | .958 | .957 |
| | 60 | ..... | 203.8 | .3861 | .977 | .974 |
| | 50 | ..... | 238.5 | .4520 | .971 | .968 |
| | 40 | ..... | 278.9 | .530 | .960 | .962 |
| | 35 | ..... | 299.7 | .568 | .950 | .951 |
| | 30 | ..... | 323.2 | .612 | .943 | .945 |
| | 20 | ..... | 377.1 | .710 | .930 | .931 |
| | 10 | ..... | 445.6 | .836 | .936 | .936 |
| | 5 | ..... | 481.1 | .901 | .925 | .923 |
| | 0 | .878 | 567.7 | 1.060 | ..... | ..... |
| N+M | 50 | ..... | 219.5 | .4282 | .885 | .882 |
| P+Q | 50 | ..... | 236.2 | .4376 | .962 | .959 |

**TABLE 7.—Tests of Blends Containing Kerosenes of Different Crudes at 20° C (68° F)**

| Oils | Percentage of lighter oil in blend | Specific gravity $\frac{15.6°}{15.6°}$C | $t$ | $\mu$ | $\frac{t}{t'}$ | $\frac{\mu}{\mu'}$ |
|---|---|---|---|---|---|---|
| N+Q | 100 | 0.806 | *33.7 | 0.0166 | | |
| | 90 | | 35.2 | .0213 | 0.965 | 0.847 |
| | 80 | | 37.6 | .0285 | .918 | .750 |
| | 70 | | 41.1 | .0389 | .848 | .673 |
| | 60 | | 46.5 | .0537 | .767 | .613 |
| | 50 | | 55.6 | .0768 | .688 | .578 |
| | 40 | | 70.3 | .1115 | .623 | .584 |
| | 30 | | 98.7 | .1739 | .604 | .566 |
| | 20 | | 149.2 | .2803 | .621 | .606 |
| | 15 | | 189.0 | .3620 | .644 | .636 |
| | 10 | | 273.3 | .534 | .764 | .761 |
| | 5 | | 384.8 | .758 | .880 | .877 |
| | 0 | .911 | 534.8 | 1.064 | | |
| P+M | 100 | .808 | *33.8 | .0171 | | |
| | 90 | | 35.8 | .0231 | .976 | .904 |
| | 80 | | 39.0 | .0324 | .959 | .848 |
| | 70 | | 43.1 | .0438 | .891 | .765 |
| | 60 | | 48.6 | .0582 | .805 | .678 |
| | 50 | | 58.1 | .0815 | .728 | .634 |
| | 40 | | 75.8 | .1215 | .667 | .652 |
| | 30 | | 107.6 | .1886 | .679 | .684 |
| | 20 | | 168.4 | .3116 | .731 | .722 |
| | 15 | | 216.8 | .3972 | .738 | .733 |
| | 10 | | 267.5 | .506 | .789 | .783 |
| | 5 | | 348.2 | .662 | .839 | .836 |
| | 0 | .882 | 593.6 | .969 | | |
| N+M | 50 | | 57.4 | .0812 | .704 | |
| P+Q | 50 | | 56.5 | .0779 | .716 | .612 |

It is seen that the naphthene base oil in Table 7 is cut to a greater extent than the paraffin base oil, but the difference is not so great as in Table 6. In both tables the blends containing component oils of the same crudes show values of the correction factors which are intermediate between the extreme values for blends of unlike crudes.

## VIII. GRAPHICAL REPRESENTATION OF RESULTS OF TESTS

Fig. 4 shows the results of tests except those of Table No. 5, Series 2, which were omitted to avoid confusion. It will be noted that the time ratio, or correction factor, is not a minimum for the 50 per cent blends, as might be expected. The points for these blends are located on vertical dotted lines, there being one blend in Espy's tests and in Series 1, and four blends in Series 3 and 4.

Assuming that the points should lie on smooth curves, Fig. 4 may be used as an indication of the reliability of the tests. Espy's tests and those of Series 1, for example, show greater irregularities in Fig. 4 than when plotted in the form of Fig. 1. While the figure is convenient for interpolation between tests in a series of blends of two given components, it is not convenient for interpolation between one series and another.

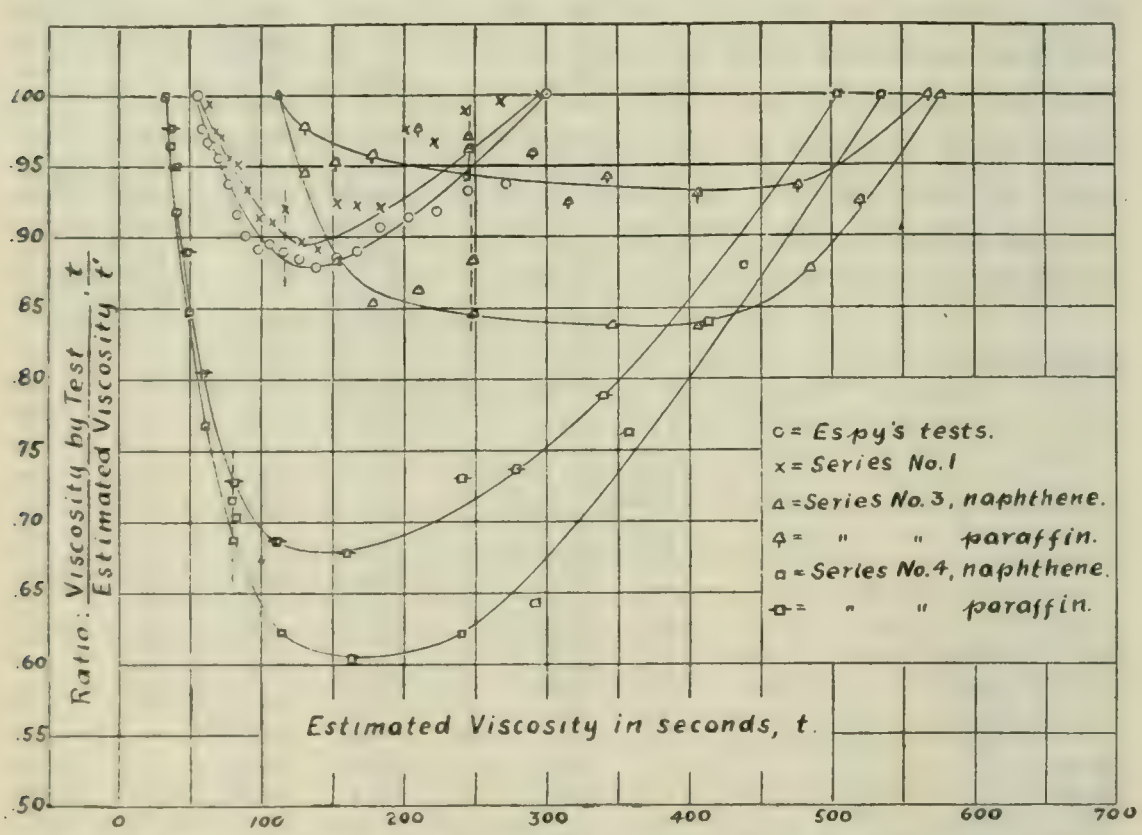


FIG. 4.—*The relation between the viscosity as determined by test, and as estimated by the logarithmic rule*

By the use of Fig. 3 the viscosity of a blend could be obtained on the assumption that it depended upon only three independent variables, the Saybolt viscosities of the two component oils and their proportions. But experiment has shown that the viscosity of a blend also depends upon the source of the crude, and it is possible that the range of boiling point should also be taken into account.

In order to reduce the number of variables and facilitate graphical representation it was decided to concentrate attention upon 50 per cent blends. If the correction factor for this blend is known the factors for other proportions may be estimated by sketching in curves similar in shape to those of Fig. 4. The variable due to source may be eliminated by using separate diagrams for naphthene and paraffin crudes, as the difference between them is not so great as to make the error in interpolating between them of seri-

ous amount. Density may be eliminated by using poises instead of Saybolt viscosities. Then the only remaining variables are the viscosities of the two component oils, for which the correction factor for a 50 per cent blend is desired.

A blend of any proportions may be considered as a 50 per cent blend of two other blends. Thus a blend containing 20 per cent of the lighter oil may be considered as a 50 per cent blend of two others, one containing 10 and the other 30 per cent of the lighter of the original components. In this case it would be necessary to reestimate the viscosity of the 20 per cent blend by equation (3) from the experimentally determined viscosities of the 10 and 30 per cent blends. The tests of Series 2, 3, and 4 were used in this manner to estimate viscosities of 50 per cent blends, and the results are shown in Fig. 5.

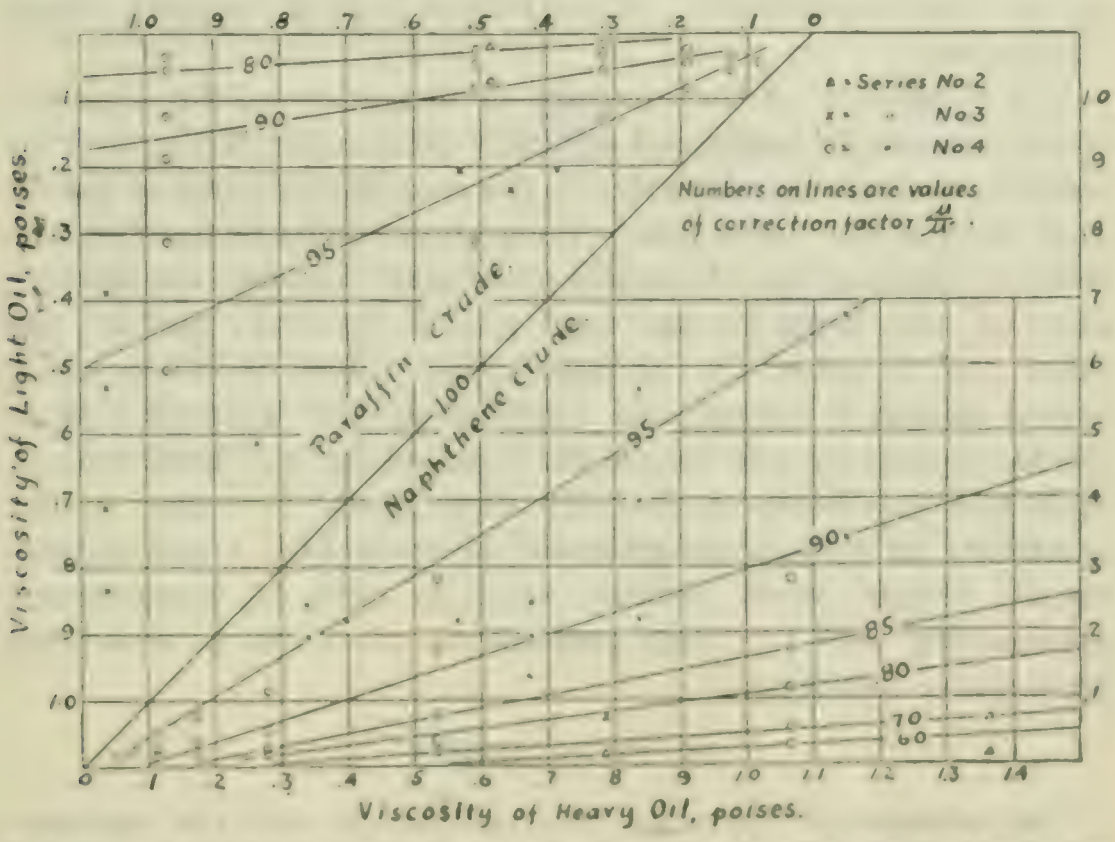


FIG. 5.—*Diagram for estimating the correction factor for viscosities calculated by the logarithmic rule*

The figure is divided into two sections by the diagonal line marked 1.00, the upper portion being for the blends P + M and the lower for the blends N + Q. In plotting the diagram each point was marked with the corresponding value of $\frac{\mu}{\mu'}$ (not shown) and the lines drawn to conform as well as possible with these values, as in making a contour map. As might be expected from Fig. 4,

the points for the upper portion of the diagram were more discordant than those for the lower. No use was made of Series 1, because the tests were less concordant and the range of viscosities was not large.

From the tests of Series 2 and 4 the errors in the logarithmic rule for estimating the viscosity of blends might at first sight appear so large as to render the rule of little value. But in actual blending operations such light diluents are not used and the errors would be much smaller. Excluding steam-engine cylinder oils or "cylinder stock," the range in viscosity is from about 750 down to 80 seconds at 100° F (37.8° C), or say 1.5 to 0.12 poise. In the extreme case, therefore, the correction factor, from Fig. 5, would be 0.75 for naphthene and 0.80 for paraffin crudes, corresponding to an error in viscosity of 33 and 25 per cent, respectively. The errors in Saybolt viscosity would be still less.

The estimation of the viscosity of blends containing cylinder stock presents an additional difficulty on account of the error in measurement of viscosities due to the change of volume of the oil after leaving the outlet tube. Espy gives results of tests on two series of blends of oils of 300 and 55 seconds' viscosity, the temperature of test being in one case 100° F (37.8° C) and in the other 210° F (98.9° C). Corresponding values in these series agreed within 1 second, and Espy apparently assumes that it would be entirely safe to use his diagram for any temperature. It is believed, however, that attention should be called to the possibility of serious disagreement between Fig. 5 and experimental results, when cylinder stock is used at temperatures approaching 100° C, unless precautions are taken to avoid the error above mentioned.

## IX. CONCLUSION

The evidence of the tests here recorded is that the viscosity of a blend can best be estimated from the rule that the logarithms of the viscosities, in poises, are additive. The determination of viscosities in poises, from Saybolt viscosities, has been discussed in previous papers. The larger the difference between the viscosities of the constituent oils the greater will be the error in the logarithmic rule, the true viscosity being less than the estimated value. For equal differences of viscosity, the error increases as the viscosity of the lighter component decreases. The true

viscosity will be greater than calculated on the assumption that fluidities are additive.

Since it was found that the error in the logarithmic rule depended upon the source of the component oils, it seemed preferable to use an uncorrected table or diagram, calculated by this rule, and give data concerning variations in the correction factor, so that each user of the diagram could select the appropriate correction factor according to the crudes to be used. Diagrams are given for finding the correction factor for 50 per cent blends of oils of any crude or any viscosity, and for then estimating the correction factor for blends of other proportions. It is believed that by this means the error in estimating the viscosity of a blend will be comparable with the error in determining the viscosity of the component oils.

WASHINGTON, January 24, 1920.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 165

# ENAMELS FOR SHEET IRON AND STEEL

BY

J. B. SHAW, Assistant Ceramic Chemist

*Bureau of Standards*

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| | 40 |
| | 44 |
| | 44 |
| | 44 |
| | 45 |
| | 45 |
| | 45 |
| | 46 |
| | 47 |
| | 47 |
| | 48 |

TECHNOLOGIC PAPERS OF THE
BUREAU OF STANDARDS, No. 165

## ERRATA

Page 7, last table, column three, line one: The values given are as in the original. Evidently they should be 0.40 to 0.60.

Page 25, line four of tabulation: The values given are as in the original. Evidently there is some error.

Page 28: The first equation should read

$$SiO_2 + F_4 = 4SiF_4 + O_2$$

Page 61, Table 4: The formula weight of boric acid should be 124. The formula weight and melted weight of cobalt oxide should be 241.

Page 62, Table 4: The melted weight of cryolite should be 288.

Page 64: The table should be as follows:

| ula | | | | | Material used | Molecular parts | Formula weight | Batch weight |
|---|---|---|---|---|---|---|---|---|
| $l_2O_3$ | $SiO_2$ | $B_2O_3$ | F | $Sb_2O_3$ | | | | |
| .20 | 1.60 | 0.50 | 1.52 | 0.10 | | | | |
| .09 | .54 | .... | .... | .... | (Feldspar, $K_2O$, $Al_2O_3$, $6SiO_2$....) | 0.09 | X996 | 90.04 |
| .11 | 1.06 | .... | .... | .... | (Borax $Na_2O$.) | 2[illegible] | X382 | 26.50 |

Page
4 5 8 9 9 10 10 10 11 11 11 12 13 13 14 15 16 16 16 18 22 22 25 25 27 29 29 30 31 33 34 34 35 37 39 40 44 44 44 45 45 45 46 47 47 48

| Formula | | | | | | | | | | Material used | Molecular parts | Formula weight | Batch weight |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_2O$ | $Na_2O$ | CaO | BaO | ZnO | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ | F | $Sb_2O_3$ | | | | |
| 0.09 | 0.62 | 0.10 | 0.10 | 0.09 | 0.20 | 1.60 | 0.50 | 1.52 | 0.10 | | | | |
| .09 | .... | .... | .... | .... | .09 | .04 | .... | .... | .... | (Feldspar, $K_2O$, $Al_2O_3$, $6SiO_2$....) | 0.09 | X556 | 50.04 |
| .... | .... | .... | .... | .... | .11 | 1.06 | .... | .... | .... | | | | |
| .... | .25 | .... | .... | .... | .... | .... | .50 | .... | .... | (Borax, $Na_2O$, $2B_2O_3$, $10H_2O$. ..) | .25 | X382 | 95.50 |
| .... | .37 | .... | .... | .... | .... | .... | 0 | .... | .... | | | | |
| .... | .33 | .... | .... | .... | .11 | .... | .... | 1.32 | .... | (Cryolite, 6NaF, $Al_2F_6$.....) | .11 | X420 | 46.20 |
| .... | .04 | .... | .... | .... | 0 | .... | .... | .20 | .... | | | | |
| .... | .... | .10 | .... | .... | .... | .... | .... | .20 | .... | (Fluorspar $CaF_2$... | .10 | X 78 | 7.80 |
| .... | .... | 0 | .... | .... | .... | .... | .... | 0 | .... | | | | |
| .... | .... | .... | .10 | .... | .... | .... | .... | .... | .... | (Barium carbonate, $BaCO_3$.....) | .10 | X197 | 19.70 |
| .... | .... | .... | 0 | .... | .... | .... | .... | .... | .... | | | | |
| .... | .... | .... | .... | .09 | .... | .... | .... | .... | .... | (Zinc oxide, ZnO.. | .09 | X 81 | 7.29 |
| .... | .... | .... | .... | 0 | .... | .... | .... | .... | .... | | | | |
| .... | .... | .... | .... | .... | .... | .... | .... | .... | .10 | (Antimony oxide, $Sb_2O_3$.....) | .10 | X287 | 28.70 |
| .... | .... | .... | .... | .... | .... | .... | .... | .... | 0 | | | | |
| .... | .... | .... | .... | .... | .... | 1.06 | .... | .... | .... | (Flint, $SiO_2$..... | 1.06 | X 60 | 60.36 |
| .... | .... | .... | .... | .... | .... | 0 | .... | .... | .... | | | | |
| .... | .04 | .... | .... | .... | .... | .... | .... | .... | .... | (Sodium nitrate, $(NaNO_3)_2$.....) | .04 | X170 | 6.80 |
| | 0 | | | | | | | | | | | | 322.39 |

# ENAMELS FOR SHEET IRON AND STEEL

By J. B. Shaw

## CONTENTS


| | Page |
|---|---|
| I. Introduction | 4 |
| II. Properties and preparation of steel for enameling | 5 |
| 1. Physical and chemical requirements | 5 |
| 2. Sand blasting | 8 |
| 3. Treatment preliminary to pickling | 9 |
| (*a*) Scaling | 9 |
| (*b*) Removing grease with caustic soda | 10 |
| (*c*) Use of proprietary cleaning compounds | 10 |
| 4. Pickling | 11 |
| (*a*) Pickling vats | 11 |
| (*b*) Pickling acid | 11 |
| (*c*) Strength of the acid | 12 |
| (*d*) Absorption of gases in pickling | 13 |
| (*e*) Manipulation of the pickling operation | 13 |
| (*f*) Electric pickling | 14 |
| (*g*) Washing after pickling | 15 |
| (*h*) Appearance of pickled steel | 16 |
| III. Raw materials for enamels | 16 |
| 1. Silica | 16 |
| 2. Feldspar | 18 |
| 3. Borax | 22 |
| (*a*) Preparation | 22 |
| (*b*) Function of borax in enamels | 25 |
| 4. Cryolite | 25 |
| 5. Fluorspar | 27 |
| 6. Barium carbonate | 29 |
| 7. Zinc oxide | 29 |
| 8. Sodium and potassium salts | 30 |
| 9. Compounds of antimony | 31 |
| 10. Effect of other constituents of enamel on the color produced by antimony oxide | 33 |
| IV. Preparation of enamels | 34 |
| 1. Mixing the raw materials | 34 |
| 2. Melting | 35 |
| 3. Tempering enamel slips | 37 |
| (*a*) Settling of the enamel | 39 |
| (*b*) Viscosity measurements | 40 |
| V. Enameling process | 44 |
| 1. Application of the enamel | 44 |
| (*a*) Slushing | 44 |
| (*b*) Draining | 45 |
| (*c*) Spraying | 45 |
| (*d*) Dusting | 45 |
| 2. Drying | 46 |
| 3. Burning enamels | 47 |
| (*a*) General description | 47 |
| (*b*) Temperature of burning | 48 |

Page

VI. Calculation of enamel formulas ..... 52
1. Methods employed ..... 52
2. Composition in terms of oxides ..... 53
3. Moisture factor ..... 57
4. Empirical formula ..... 58
5. Calculation of empirical formula from chemical analysis ..... 60
6. Calculation of empirical formula from batch weights ..... 62
7. Calculation of batch weights from the empirical formula ..... 63
8. Use of curves in calculating formulas from batch weights ..... 65
VII. Physical properties of enamels ..... 71
1. Introduction ..... 71
2. Resistance to sudden change of temperature ..... 71
3. Resistance to abrasion ..... 73
4. Controlling the toughness of enamels ..... 74
VIII. Resistance of enamels to chemical action ..... 74
1. Introduction ..... 74
2. Action of glass ..... 75
3. Work of Orton ..... 77
4. Work of Shaw—first investigation ..... 78
5. Work of Shaw—second investigation ..... 81
(*a*) Enamels tested ..... 81
(*b*) Results of acid tests ..... 81
(*c*) Opaque enamels versus translucent enamels ..... 85
6. Work of Landrum ..... 85
7. Action of various acids on enamels ..... 87

## I. INTRODUCTION

Within the last 20 years the ceramic industries of the United States have made great improvements in the quality of their products, due to the abandonment of the rule-of-thumb methods which marked the beginning of the industries and to the application of scientific principles in the manufacturing processes. Many volumes have been written describing the results of extensive investigations of cause and effect; as a result of these extended researches both in factory and laboratory the sum total of known facts regarding the silicate industries has been greatly augmented. Therefore, the physical and chemical properties of ceramic products can be modified and largely controlled at will. By correlation of data obtained by many different investigators manufacturers of ceramic wares are not only eliminating waste in their factories, but are also developing their products to a high state of perfection. It should be said, however, that, while much has been learned, very much more is to be learned even in the most advanced of the industries.

From the standpoint of mechanical equipment the sheet iron and steel enameling industry has been probably the most progressive of all ceramic industries in the United States. The presses and machinery used for working the steel and forming the shapes

are unsurpassed in ingenuity by those used in any other industry, and are constantly being improved. In this respect the sheet-metal enameling industry of this country has led the world.

In the strictly ceramic lines of the industry having to do with the preparation and application of the enamels progress has been less rapid. Up to a few years ago there was very little cooperation. There was very little research work carried on, and this little was seldom reported in print. Very recently there has been a decided change in this respect. Representatives of the enameling industry have been joining the ceramic technical societies; have been contributing rather liberally to the journals of these organizations; and have been showing a decided interest in developing the technology of sheet-metal enameling. The leading manufacturers of the country are realizing that the sheet-iron enameling industry has reached the limit of development possible, so long as it depends upon formulas rather than upon men with the technical training which will enable them to improve and manipulate these formulas to meet varying conditions. The sum total of known facts about enamels and their application is very small. There is room for enormous expansion and improvement in the industry, and this can be accomplished only by active cooperation and research. In collecting data for this paper an effort has been made to obtain reliable and authentic information wherever available and to correlate it in such a manner as to shed some light on the problems encountered by enamelers.

## II. PROPERTIES AND PREPARATION OF STEEL FOR ENAMELING

### 1. PHYSICAL AND CHEMICAL REQUIREMENTS

In commenting upon the kind of steel used in European practice, Julius Grünwald says: [1]

> For acquiring a well-finished article the use of first-class, box-heated, doubly forged basic Martin steel is indispensable. Inferior kinds of steel, such as are often used for some cheap folded articles, are in reality of no advantage when one considers the greater percentage of imperfect goods produced and the insignificant difference in price between the doubly forged and the singly forged varieties of sheet steel. Consequently the manufacturers use almost throughout only the very best German brands, which are entirely equal to the English forged preferred earlier. The following is regarded as a favorable composition for a good forged steel

| | Per cent |
|---|---|
| Carbon | 0.05 to 0.08 |
| Phosphorus less than | .03 |
| Manganese | .25 to .35 |
| Silicon, small amounts | .02 |

[1] Grünwald, J., Technology of Iron Enameling and Tinning, Griffin, 1913.

The strength test must show the following results:

| | |
|---|---|
| Coefficient of tenacity | 35 to 38 kg/mm² |
| Coefficient of elasticity | 30 to 35 per cent |
| Coefficient of contraction | 60 per cent |
| Specific gravity | 7.6 to 7.8 |

It is generally accepted as a fact that in no other country has the manufacture of steel reached a higher state of refinement than in the United States. Some of the largest manufacturers in the country supplying the enameling trade have the following to say with regard to steel for enameling purposes:

No special grade of steel is manufactured to be used exclusively for enameling purposes, but steel manufacturers do make a steel, used quite extensively by the manufacturers of enameled ware, which is particularly adapted for deep-stamping purposes, and in which the different impurities are kept low to avoid excessive breaking. The annealing of such steel also has an important bearing on the quality.

It has been found that standard soft steel for deep-stamping purposes, made by either the Bessemer or open-hearth process (depending largely on the severity of the drawing operation which it is required to meet) and having about the following composition, seems to give the best results when properly treated while undergoing processes:

| | Per cent |
|---|---|
| Carbon | 0.08 to 0.12 |
| Phosphorus | .040 and under |
| Manganese | .30 to 0.50 |
| Sulphur | .05 and under |
| Silicon | .025 and under |

There is nothing peculiar in the rolling of the material into sheets, the regular practice of alternate heating and rolling being followed until the required gage is obtained. The gages used are generally within the range of No. 20 to 28 United States standard gage.

After rolling, the packs, which contain a number of sheets, are sheared, and the sheets are opened or separated; then they are subjected to a pickling operation, embodying an exposure of approximately five minutes in a bath of sulphuric acid containing approximately 5 per cent free acid, at a temperature of approximately 180° F. This is for the purpose of entirely removing all mill scale formed during the rolling process.

When the pickling operation has been completed, the sheets are transferred to a water bath and by agitation therein freed from adhering acid to the greatest possible extent. The sheets are then subjected to an annealing operation, under cover, at a temperature of approximately 1400° F for a period of from 14 to 16 hours.

When annealed and cooled the sheets are inspected, and those rejected which are determined to be unsuitable for the stamping and enameling operation. These rejections are confined entirely to mechanical defects, such as thick edges, which interfere with satisfactory drawing, and surface defects and imperfections which might interfere with this or with the enameling operation.

Practically pure iron is a recent development in the steel industry. The operations required in making it are the same as those in making any other grade of open-hearth steel, but due to the fact that the product is higher in iron (Fe) and lower in other ingredients which go to make up the body of other steel, the process requires higher temperatures for melting and more inten-

sive open-hearth treatment to eliminate the phosphorus, manganese, sulphur, and silicon.

This iron has a smooth surface and is uniformly free from blisters and irregularities in texture. Its high iron content and low phosphorus and silicon contents make it very ductile, and therefore well adapted to deep drawing. In view of the fact that much of the loss in the enamel industry results from breakage in drawing, this factor is one of importance. As regards the ability of this iron to take a coating of enamel better than other steel, no exact data are available from which to judge. Theoretically, one disadvantage which it has is the smoothness of the surface. However, it has been used successfully in a number of enameling plants.

A manufacturer of heavy-gage, enameled-steel containers made comparative tests on steels of the following compositions:

| No. | Carbon | Sulphur | Phosphorus | Manganese |
|---|---|---|---|---|
| 33568 | 0.12 | 0.018 | 0.008 | 0.35 |
| 33457 | .10 | .025 | .010 | .42 |
| 34421 | .15 | .022 | .009 | .33 |
| 33613 | .13 | .025 | .011 | .46 |
| 33590 | .10 | .023 | .009 | .35 |

The five steels were selected for test with a view to finding one which could combine qualities meeting several requirements, namely, flanging, welding, forming into different shapes, and enameling.

It was found that about 10 per cent of the sample sheets which were very good for enameling broke down under the other tests. No. 34421 was selected as most satisfactory and was adopted for use. Several thousand tons of it have since been enameled with excellent results. Steel having the other four compositions has many defects.

R. D. Landrum [2] gives the following as the best composition of steel for enameling purposes:

| | Per cent |
|---|---|
| S | 0.040 to 0.050 |
| P | .030 to .090 |
| Si | .01 |
| Mn | .060 to .040 |
| C | .10 |

The following compositions are recommended or sold for use:

| Carbon | Phosphorus | Manganese | Sulphur | Silicon | Authority |
|---|---|---|---|---|---|
| 0.10 | 0.030 to 0.090 | 0.040 to 0.060 | 0.040 to 0.050 | 0.01 | Landrum |
| .15 | .009 | .33 | .022 | | A manufacturer of heavy containers |
| .08 to 0.12 | .040 and under | .30 to .50 | .05 and under | .025 and under | American practice |
| .05 to .08 | Less than .03 | .25 to .35 | | .02 | Grünwald |

[2] Landrum, R. D., Methods of Analysis for Enamel and Enamel Raw Materials, Trans. Am. Ceram. Soc., 12, p. 174.

The table includes a comparatively wide range of compositions, showing a wide diversity of opinion as regards the proper composition of steel for enameling purposes.

One is led to the conclusion that the chemical composition of the steel has no important bearing on its ability to take and hold a coating of enamel successfully. This seems quite reasonable in view of the fact that cast iron, containing large quantities of silicon, phosphorus, manganese, and carbon, is easily enameled, and steels of great variety in composition, running from those highest in matter other than iron to the purest wrought iron, are successfully enameled for various purposes.

Experience in enameling many different kinds of ware confirms the above conclusion. There is only one type of defect in enameled ware that can properly be attributed to bad steel, and that is the blistering which comes from a pocket of gas or slag being rolled into the sheet. These blisters result from poor steel and very frequently reveal themselves during the pickling operation. It frequently happens that the enameler, in trying to clear himself of the blame for defective ware, attributes the trouble to defective steel. To make a cry of poor steel is an easy way to shift the responsibility for poor ware; but if a piece of steel is free from blisters and is properly cleaned, it is only a remote possibility that any defects in the enamel coating can be properly attributed to it, regardless of its chemical or physical properties.

When it comes to consideration of the action of steel in drawing and stamping, the chemical and physical properties are highly important. In order to stand deep drawing, steel must possess a high degree of ductility and high tensile strength. These properties are imparted to the steel by giving it the proper chemical composition and the proper treatment during the process of manufacture.

### 2. SAND BLASTING

The preparation of the steel for enameling consists in giving it such treatment as is necessary to leave a clean surface, free from any foreign matter that will injure the enamel when applied and burned. The treatment required depends upon the nature and size of the piece of ware and the kind of foreign matter that is to be removed.

The sand blast is used in cleaning large ware and such as can not be easily cleaned by pickling. When the sand blast is used, no other treatment is required, since grease, rust, and any other

foreign matter is readily removed by it. This is the most effective method of cleaning steel and one that gives an excellent surface for enameling. For small pieces it is much more expensive than pickling, and it is economical only in making large pieces or special shapes of comparatively high value.

### 3. TREATMENT PRELIMINARY TO PICKLING

Nearly all light steel ware is cleaned by the pickling process. The preliminary treatment before the ware is placed in the pickling acid varies. Grease and carbonaceous matter must be removed from the ware before placing in the pickling solution, and three general methods are in use for doing this; scaling, washing in caustic alkali solutions, or the use of proprietary cleaning compounds.

(*a*) SCALING.—Scaling or heating the ware to redness is the method most generally employed. During the process of shaping the ware from the sheet of steel it invariably collects grease from machinery and workmen's hands, and one method of removing such carbonaceous matter is to burn it off. Especially is this the case when handling large numbers of small pieces. To do this, the ware should be carefully stacked on grates in such a manner as to admit free access of air to all parts of every piece of ware. Care must be taken to prevent flat surfaces from coming into contact with each other, and space must be provided between the different pieces of ware to admit sufficient air to completely oxidize all carbonaceous matter present. It must be remembered that the heat treatment forms an iron scale which must subsequently be removed by acid, and consequently the time and temperature should not be carried beyond that necessary to burn off the oil.

The primary object in scaling is to burn off the carbonaceous matter, but this heat treatment does undoubtedly have the effect of changing the structure of the steel and relieving strains set up during the forming. Grünwald [3] attaches considerable importance to the benefit derived during this heat treatment through liberation of the strains set up during the forming of the ware. While there is ample proof that these strains do exist and are vital factors affecting the property of the steel for drawing, there is no evidence to show that they affect the ware as regards the appearance of enamel or its adherence to the metal. As evidence that these strains do affect the enamel, it is generally pointed out that the

[3] Grünwald, J., Technology of Iron Enameling and Tinning.

angles and sharp corners are the most difficult places on which to make enamel stick; but precisely the same thing is true of cast-iron enamels, in which case no strains exist in the corners any more than those which may exist on the flat surfaces.

As a result of an extensive series of experiments on pickling operations, Grünwald concluded that the proper temperature for heating the ware in scaling is between 650 and 750° C. If the temperature is much below 650° C, the oil will not be completely burned off. If the temperature exceeds 750° C, the amount of scale formed on the surface is excessive, increasing unnecessarily the cost of pickling. He shows that the time required for pickling increases with the duration and temperature of heating the ware; thus only 3 minutes are required for pickling with hydrochloric acid, 10° Baumé, a sheet-iron disk that has been heated at 760° C, while 14 minutes are required for pickling a sheet heated for the same length of time at 940° C. When sulphuric acid, 110° Baumé at 60° C is used, the time required for pickling is increased.

(*b*) Removing Grease with Caustic Soda.—Caustic soda or potash may be used for removing fatty materials, especially if they are present in small amounts. In this process the steel article is immersed in a boiling solution of caustic soda or potash and allowed to remain for a few minutes. It is then taken out and washed free from alkali in clear water. This precaution is necessary because the adhering alkali solution would rapidly neutralize the pickling acid into which the steel is next placed for the removal of rust and other deleterious impurities.

(*c*) Use of Proprietary Cleaning Compounds.—There are on the market a number of prepared chemical cleaners which may be substituted for caustic soda and which give excellent results in the removal of grease from ware to be enameled. These cleaners may be composed of one or several of the following materials: Sodium hydroxide, sodium carbonate, ammonium carbonate, borax, trisodium phosphate, sodium silicate, soaps, and rosin, which, in the presence of caustic alkalies, forms soaps.

This method of removing grease with chemicals should not be employed in cleaning ware which becomes coated with heavy mineral oils during the manufacturing process, because it is difficult to remove these oils. On large flat pieces and such as are not handled much during the shaping, the amount of oily matter to be removed is small, and this process can be used to advantage in such cases.

### 4. PICKLING

After the oil and carbonaceous matter have been removed from the surface, it is necessary to remove all rust and oxide of iron. As has been noted, in the scaling and annealing of the steel there is always more or less oxide of iron formed on the surface, and this must be removed before the ware can be successfully enameled. The pickling solution used is one of either sulphuric or hydrochloric acid.

(*a*) PICKLING VATS.—One of the most troublesome problems in the enameling plant is to get satisfactory vats for holding the pickling solution. General practice is to use double tanks made of soft pine with a space of about 2 inches between the inner and outer walls. This space is filled with pitch, which is melted and poured into place. This is probably the most satisfactory form of tank for use where the acid is not heated, but if a hot acid bath is used the pitch will soften and allow the acid to work its way through to the outside. Wooden tanks lined with sheet lead have been tried, but they are expensive and the rough treatment to which they are subjected in placing ware in them and taking it out soon destroys them.

A satisfactory tank for enameling work is made from good quality cypress, at least 2½ inches thick and braced throughout with wood. If iron bracing is used, it should be renewed at frequent intervals. The threads on iron rods are very rapidly destroyed by acid vapors, and when the bracing gives way the tank very soon begins to leak. It is almost impossible to stop such a leak. If a tank is made of cypress and is kept well braced it will last almost indefinitely.

(*b*) PICKLING ACID.—The question of what is the best acid to use for pickling steel is a mooted one. Both sulphuric and hydrochloric (muriatic) acids are used, and there seems to be little choice between them when everything is considered. Sulphuric is undoubtedly the cheaper, but it must be heated to get it to work as rapidly as does the hydrochloric when cold, and the fumes arising from hot sulphuric acid cause great inconvenience to the workmen. Proper precautions may be taken to carry off the fumes, and this not only has the advantage of saving the workmen from discomfort, but also keeps the acid fumes out of the other parts of the factory, and thus prevents corrosion of metal parts. Even when cold hydrochloric acid is used it is of great importance that the pickling room be isolated from the

other departments, and it is also advisable to use fans to draw off the acid vapors.

Niter cake has come into extensive use for pickling in recent years. It is a by-product obtained in making nitric acid from sodium nitrate and sulphuric acid, according to the following reaction:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

The acid-sodium sulphate or niter cake is shipped in bulk, thereby avoiding the use of carboys. Sulphuric acid is the active agent in using this material, it being liberated when the salt is dissolved in water. It is necessary to heat the pickling solution in this case, as in the use of sulphuric acid.

Acid vapors from the pickling room are injurious both to ware which has not been coated with enamel and to ware which has a coat of enamel on it, but requires a subsequent coating. If ware which has not been enameled is subjected to the acid vapors it is likely to rust, and this will cause defective ware. If ware coated with enamel is subjected to the acid vapors the enamel will decompose, forming a white deposit, and when attempts are made to dip such ware for a second application of enamel it will be found very difficult to get a uniform coat of enamel over the surface.

A useful expedient adopted at some plants is to cover the surface of the acid with a film of flour, bran, or other similar ground mill product. It has been found that by sprinkling a few handfuls of wheat flour over the tank daily, practically all inconvenience from acid vapor is eliminated. These organic substances, due to their charring by the acid, form a blanket of charcoal and foam over the acid, which retards the expulsion of the hydrogen gas and acid fumes. It is claimed by manufacturers of some of these compounds that the retention of the hydrogen gas in the bath accelerates pickling, but experience of those using these materials apparently shows the contrary to be true. In a number of cases the use of these materials has been discontinued, due to the "killing" of the acids after their use.

(c) Strength of the Acid.—The subject of strength of acid necessary to give the highest efficiency has been studied by several investigators. The work of Grünwald[4] in this connection is worthy of note. He found that HCl at 17° Baumé gave maximum speed when cold, and at 22° Baumé gave maximum speed

[4] Grünwald J., Technology of Iron Enameling and Tinning.

when heated to 60° C. He concludes that sulphuric acid is superior to hydrochloric because it can be produced at higher concentration, sulphuric being obtainable at 60 to 66° Baumé, while the maximum concentration for hydrochloric is 24° Baumé. He names 60° C as the temperature at which the highest efficiency is obtained in pickling.

(*d*) Absorption of Gases in Pickling.—Treischel [5] has shown that the amount of blistering encountered in enameling sheet steel can be greatly reduced by the substitution of sand blasting or of pickling with 3 per cent acid solutions for pickling with 10 per cent acid solutions. He attributes the blistering to the absorption of hydrogen by the steel during pickling in strong acid solutions.

(*e*) Manipulation of the Pickling Operation.—Ware should be carefully placed in the pickling acid so as to prevent pockets of air being entrapped in corners and so as to avoid the contact of flat surfaces with each other. It is important that the pickling operation be not prolonged unnecessarily, since this not only results in waste of acid but also reduces the thickness of the metal. When it is found that a spot on a piece of ware has not been thoroughly pickled because of a pocket of air or because two flat pieces have been in contact with each other, a repickling, for about the same length of time as the original article required, is necessary. This results in a loss of acid and variation in structure of the surface which may prevent the enamel from adhering properly.

The general practice in enameling plants is simply to place the ware in the acid and allow it to remain there until pickled. Sometimes the operation requires 30 to 40 minutes. This is bad practice from every point of view. It results in loss of time, loss of acid, and a lack of uniformity of structure in different parts of the surface. In steel-plant practice the metal is continually agitated by a mechanical device during the pickling operation, and it would be decidedly to the advantage of enameled-ware manufacturers if they adopted a similar practice. The agitation of the bath insures a very much higher efficiency in the pickling operation than is possible to obtain when the ware is merely left quiet in the acid. This can be accomplished either by moving the ware by a mechanical device such as is in general use in steel plants or by agitating the solution itself. Agitation not only accelerates the

[5] Treischel, Chester, The Cause and Control of Blistering in Sheet Steel Enameling. Jour. Am. Ceram. Soc., 2, 774.

rate of chemical action, but, what is still more important, it accelerates the mechanical action of removing the scale.

The removal of scale from a sheet of steel in pickling is very largely a mechanical action. The amount of scale taken into solution during the operation is very small, by far the larger percentage being removed by the acid penetrating beneath the scale and dissolving the surface layer of steel. During the pickling operation many flakes of scale can be seen floating in the solution, and a sludge consisting of iron scale very soon collects on the bottom of the tank. Of course, the acid continues to act upon the scale after its removal from the steel, but this is the case with only strong acid solutions and not with weak solutions. The higher form of iron oxide, $Fe_2O_3$, is more easily acted on by the acid than are the ferrous oxides, $Fe_3O_4$ and FeO.

The loss of acid due to unnecessary action on the sludge which settles to the bottom of the tank has been considered of sufficient importance by some to justify employing a method for its removal from time to time. Grünwald [6] mentions a method proposed by Cowper-Cole, which consists in electrolytic separation. He suggests decantation of the solution as being simpler. It seems doubtful if this loss will justify the separation by either means. There certainly will be no saving if the solution is in continual use, because the amount of scale deposited from a single batch of ware is sufficient to thoroughly contaminate the solution. If, however, the acid is to be allowed to stand for some time it should be decanted into clean carboys or a clean tank, thereby preserving its strength for use when needed.

(*f*) Electric Pickling—The electric pickling process consists in passing an electric current through the acid during pickling, using the iron to be pickled as the cathode. It offers some advantages over ordinary chemical pickling and has long been advocated as a cheaper process, but it has not been extensively adopted as yet even by steel manufacturers. Some advantages of the process are: (1) It uses less acid per unit area of iron pickled. (2) It is a far more rapid process than ordinary pickling. This difference becomes greater as the amount of scale to be removed increases. (3) Electric pickling in cold acid takes about the same time as ordinary pickling in hot acid. This makes it possible to avoid the injurious effect of hot acid vapors on workmen and machinery.

[6] Grünwald, J., Technology of Iron Enameling and Tinning.

(*g*) Washing After Pickling.—When steel is properly pickled no scrubbing will be necessary to remove the scale. The practice of scrubbing ware in water after taking from the acid bath should be condemned in all cases. While scrubbing will not hurt a piece of properly pickled steel, provided it is done under water, the fact that it needs such treatment is an indication that it is not properly pickled. If the acid has not loosened the scale from the steel so that ordinary rinsing in water will wash it off, it will be very imperfectly removed by scrubbing with a brush or sand. Objection to scrubbing also arises from the fact that workmen will not keep the ware under water during the operation, and steel wet with water containing traces of acid rusts very rapidly. Consequently, portions of the ware which come in contact with the air during the scrubbing operation become coated with a film of iron rust, which is very detrimental to the future enameling operations. The proper procedure, in case a piece of ware comes from the pickling tank with scale still adhering which would require scrubbing to remove it, is to replace it in the pickling tank and allow the acid to remove it.

An ample supply of clean running water should be available for washing the ware after it comes from the pickling bath. If the ware is thoroughly washed in water, practically all acid can be removed. In making any but one-coat ware, however, it is not good practice to dispense entirely with the soda bath which ordinarily follows the bath in fresh water. Even with the most thorough washing in water it is impossible to prevent some of the acid going over to the next tank, and a very small amount of acid left on a piece of steel will cause rusting which will give serious trouble when the first coat of cover enamel is burned. Therefore, after washing the ware in clean water it should be immersed in a boiling solution containing a small amount of alkali. The solution should not be strongly alkaline, because upon drying the alkali will crystallize and be deposited in large amounts in corners and at points where the solution runs when the ware is set up to dry. The deposit will decompose when the first coat of enamel is burned and is liable to cause a defective piece of ware. It should be sufficiently alkaline to give a distinct reaction with litmus paper and should be frequently tested and fresh alkali added when required. It is better to add a little soda ash three or four times a day than to add a larger amount to the solution at one time.

The steel as it comes from the boiling soda solution will usually contain sufficient heat to insure rapid drying, but to prevent rusting it should be placed in a drier and dried almost instantly.

(*h*) Appearance of Pickled Steel.—It is generally supposed that steel which has been perfectly pickled should present a perfectly clean, bright surface similar to that obtained by scratching with a file or by sand blasting. The impression is erroneous, however, and may lead to trouble. A piece of steel which comes from the pickling room with a clean appearance should be looked upon by the enameler with suspicion as an indication that the soda bath is very weak and the acid is probably not all neutralized. When the steel enters the soda bath it is coated with a solution of ferric chloride, and if the soda solution is sufficiently active there will be formed a precipitate of ferric hydroxide, which floats in the soda solution. When the ware is taken out, a film of the hydroxide will be left on the surface and will impart a brown color to the ware when dry. This dirty brown color, therefore, is an indication that the ware is free from acid or rust resulting from unneutralized acid.

## III. RAW MATERIALS FOR ENAMELS

The raw materials ordinarily used in the making of enamels for sheet iron are the following:

Silica:
- Sand
- Ground quartz

Feldspar
Borax
Cryolite (natural and artificial)
Fluorspar
Barium carbonate
Zinc oxide
Sodium and potassium salts
Compounds of antimony
Bone ash
Manganese dioxide
Cobalt oxide
Nickel oxide
Copper oxide
Clay
Tin oxide

### 1. SILICA

All enamels may be considered as silicates or borosilicates. Hence in enamels, as in most glasses, silica ($SiO_2$) may be regarded as the fundamental ingredient. In enamels it is derived chiefly from flint, quartz, and feldspar.

Flint is hard opaque material of a specific gravity ranging from 1.9 to 2.3, usually more or less colored by impurities. It consists mainly of silica in the amorphous form, partially hydrated, but usually contains some crystalline silica. In many of the deposits in the United States the material contains considerable iron oxide, which renders it unfit for use in white enamels. There are deposits in the South which could probably be used satisfactorily, as the

silica in these is almost entirely amorphous, and the material burns to a pure white color. English and French flint are imported and used to some extent.

Quartz is the most common crystalline variety of silica. It is very abundant and is found in a high degree of purity in quartzites and white sandstones. It is hard, is transparent when pure, and has a specific gravity of 2.66. Pure grades of quartz are ground and furnished to the enameler in powdered form. The term "flint" is frequently applied to ground quartz, but the two materials should be distinguished.

Sand is identical with quartz in chemical and physical properties, and is also obtainable in a quite pure state.

While the pottery industry has long recognized a very material difference in the results obtained by the use of quartz and flint in both bodies and glazes, this difference has not been generally recognized by enamelers. It is usually supposed that the form in which the silica is added to the enamel is unimportant, since it is all thoroughly melted to a glass in the smelter, and the final product is the same if all the silica is taken into solution. The form of the silica, however, in both ground-coat or white enamels, should be considered. It should be remembered that the enameler has incorporated in his melt certain materials which will perform their function only in case the smelting is stopped at the right time. This is especially true of white enamels, but to some degree also of ground coats. One of the chief differences in the three forms of silica mentioned is in the rates at which they combine with or dissolve in other materials during the melting of the batch. Amorphous flint, if ground to equal fineness, combines more readily than powdered quartz, while the coarser sand grains combine less readily than either. It follows, therefore, that the time and the temperature required for melting are materially affected by both the condition and the fineness of the silica. These variations in melting conditions, in turn, have a decided effect upon the enamels in respect to those ingredients which may lose their value through excessive heat treatment in the smelter. Thus, cryolite, antimony oxide, and tin oxide give their maximum value as opacifiers with minimum heat treatment in the smelter. The form and fineness of the silica should therefore be carefully watched and allowed for in compounding the batch.

All these forms of silicia may be used with good results, but experience has shown that in the same enamel a smaller quantity

of sand than of powdered quartz should be used. Similarly, less quartz than flint should be used, but the difference in this case is less than in the former. Flint is likely to carry a high percentage of moisture, especially when just received. This should be regularly determined and allowed for in the batch.

### 2. FELDSPAR

From a mineralogical standpoint feldspars may be divided into three classes:

1. Potash feldspar, including orthoclase and microcline; composition, $KAlSi_3O_8$ or $K_2O,Al_2O_3,6SiO_2$; specific gravity, 2.54 to 2.56.

2. Soda feldspar, albite; composition, $NaAlSi_3O_8$ or $Na_2O,Al_2O_3,6SiO_2$; specific gravity, 2.605.

3. Lime feldspar, anorthite; composition, $CaAl_2Si_2O_8$ or $CaO,Al_2O_3,2SiO_2$; specific gravity, 2.765.

In addition there are various mixtures of these varieties—anorthoclase, which consists of equal parts of potash feldspar and soda feldspar, and the soda-lime or plagioclase feldspars, which vary in composition from 6 parts of soda feldspar and 1 part of lime feldspar, to 1 part of soda feldspar and 6 parts of lime feldspar. As obtained for commercial purposes the materials are never pure, but contain more or less of a mixture of the different varieties, as well as excess silica and other minerals.

Information relative to feldspar deposits and the composition and properties of the materials may be found in references cited below.[7] Analyses of some commercial feldspars given by Bastin [8] are shown in the accompanying table.

**TABLE 1.—Analyses of Some Commercial Feldspars**

| | (a) | (b) | (c) | (d) | (e) | (f) |
|---|---|---|---|---|---|---|
| $SiO_2$ | 64.7 | 64.98 | 66.23 | 65.95 | 76.37 | 65.87 |
| $Al_2O_3$ | 18.4 | 19.18 | 18.77 | 18.00 | 13.87 | 19.10 |
| $Fe_2O_3$ | ..... | .33 | Trace | .12 | ..... | ..... |
| $CaO$ | ..... | Trace | .31 | 1.05 | .26 | .20 |
| $MgO$ | ..... | .25 | None | Trace | None | None |
| $K_2O$ | 16.0 | 12.79 | 12.09 | 12.13 | 5.24 | 12.24 |
| $Na_2O$ | ..... | 2.32 | 3.11 | 2.11 | 3.74 | 2.56 |
| $H_2O$ | ..... | ..... | ..... | ..... | .30 | .64 |
| Loss on ignition | ..... | .48 | ..... | ..... | ..... | ..... |
| | 99.1 | 100.33 | 100.51 | 99.36 | 99.78 | 100.61 |

[7] Ries, H., Bull. [illegible] and 90, U. S. Bur. of Mines; Bastin, E. S., Bull. 420 and 445, U. S. Geol. Survey; [illegible], H. E., Bull. 92, Canada Department of Mines; Galpin, S. L., Bull. 30, Georgia Geol. Survey.

[8] See [illegible]

The mineral deposits from which most commercial feldspar is obtained are called pegmatite. This term includes deposits varying in composition from nearly pure feldspar with a little quartz as impurity to a mixture containing a little feldspar with a large amount of other minerals.

Pegmatites are coarsely crystalline granites in which feldspar and quartz are the chief constituents. The other constituents of the granite in which the pegmatite is an intrusion may be totally absent or replaced by rare minerals. Sometimes the constituents of these dykes of pegmatite are separated into distinct bands in such a manner as to make it possible to obtain feldspar in commercial quantities absolutely free from other minerals, but in most cases the feldspar and quartz are too intimately associated to admit of any such possibility. In mining such material, the undesirable minerals which are sufficiently coarsely crystalline to be distinguished are sorted out, and the resulting product of the mine is necessarily a feldspar containing more or less quartz and other minerals.

Certain ceramic industries, notably the pottery industry, have insisted upon getting pure feldspar, and the producers of this material have attempted to supply the demand; as a result, there are on the market three grades of feldspar, termed "grades 1, 2, and 3," according to the purity of the material.

Referring to the demand for pure feldspar, A. S. Watts[9] makes the following statements:

> That the present demand for a pure feldspar in many of the industries is unwarranted is evidenced by the practice both in England and throughout continental Europe.
>
> The enormous white-ware industries of Staffordshire, England, are dependent upon the coarse granites or pegmatites of Cornwall for their feldspathic material. This district does not produce any pure feldspar, but only material which is a mixture of feldspar and quartz, with minor amounts of other materials. The success which has attended the use of this material is indicated by the fact that enormous quantities of crude Cornwall stone are annually imported into the United States for manufacturers who find it more satisfactory for their purpose than any of the American feldspars.
>
> In France the supply of feldspar is limited, indeed, and the famous wares of Limoges are to-day made from the semiweathered pegmatites of the St. Yrieix district. These are crushed and pulverized by wet grinding, and to them are added what additional kaolin and flint are necessary to produce the desired strength for molding and the demanded translucency when fired. The feldspars of Scandinavia are in reality pegmatite, if one may judge from the analyses obtainable.
>
> The foregoing indicates that deposits of pure feldspar are no longer available for use of the European manufacturer, and he has found it possible to produce an equally satisfactory ware from a mixture of feldspar and such other impurities as are not actually injurious when the material is properly prepared.
>
> Toward this same condition the American user of feldspar is rapidly approaching, and conditions are not improved by ignorance of the gradual change that is occurring.

[9] Watts, A. S., Bull. 92, U. S. Bur. of Mines, 1916.

or by imagining that the same quality of material is being used as when the deposits were first opened.

The aim of the foregoing statements on feldspar is to show: (1) that there are several different kinds of feldspar, each having characteristic properties of its own; (2) that the nature of the deposits from which feldspar is obtained precludes the possibility of obtaining in large amounts pure feldspar of any one kind; (3) that feldspar with quartz ($SiO_2$) as the only impurity in appreciable amounts is readily obtainable, but that the ratio of feldspar to quartz even in the same deposit varies widely; (4) that pure feldspar is not a necessity to obtain good results, provided the impurities are not themselves detrimental to the ware in which they are incorporated.

While this last statement was intended to apply to white-ware bodies, it can certainly be correctly applied to feldspar for sheet-iron enamel purposes. There is no limit to the degree in which feldspar and flint can vary in the enamel mixture, provided the fluxing elements of the feldspar are supplied from other sources when the feldspar is replaced by flint. In discussing European enameling practice, Grünwald [10] gives the following table showing the ratios of feldspar to quartz in the raw mixtures for enamels:

| Ground coat | Common white | Soft white | Acid-proof white | White for cast iron | Powdered white | Blue |
|---|---|---|---|---|---|---|
| 25:21 | 15:30 | 25:9 | 6:47 | 39:0 | 26:0 | 29:18 |
| 26:18 | 21:19 | ..... | 13:36 | 31:19 | ..... | 34:26 |
| 28:16 | 20:28 | ..... | 17:40 | 26:13 | ..... | 38:23 |
| 31:20 | 27:14 | ..... | ..... | 42:0 | ..... | 40:0 |
| 40:1 | 30:8 | ..... | ..... | 46:0 | ..... | 57:8 |
| 40:3 | 34:19 | ..... | ..... | ..... | ..... | ..... |
| ..... | 39:0 | ..... | ..... | ..... | ..... | ..... |

While the table indicates wide limits of variation, it will be noted that in all cases some feldspar is used, and in nearly all cases the feldspar exceeds the flint.

A number of formulas which have been successfully used in America show the following ratios between feldspar and quartz:

| Ground coat | Common white | Acid-proof white | White for cast iron | Blue |
|---|---|---|---|---|
| 1.6:1 | 1.3:1 | 0:1 | 2:1 | 0.90:1 |
| 1.0:1 | 1.1:1 | :1 | 1:1 | 1.0:1 |
| 1.1:1 | .9:1 | 1:1 | 1:0 | .70:1 |
| .9:1 | .9:1 | ..... | ..... | ..... |
| .9:1 | .75:1 | ..... | ..... | ..... |
| 1.0:1 | ..... | ..... | ..... | ..... |

It will be seen that American practice differs slightly from European in that the feldspar content is frequently less than the flint and the ratio generally runs close to 1:1.

[10] Grünwald, J., Raw Materials of the Enameling Industry, Trans. by H. H. Hodgson Griffin; 1914.

The basis of all enamels is $SiO_2$, and, as was said in discussing silica, the nature of the enamel is materially influenced by the source from which the silica is obtained. While in compounding sheet-iron enamels the chief source of silica is flint or quartz, still a large amount of silica is added in the form of feldspar, not only as impurity in the feldspar, but as part of the mineral itself. As is indicated by the chemical composition of feldspar, every 100 pounds of it incorporated in the enamel carries with it about 65 pounds of $SiO_2$. While it is not impossible to replace a part or all of the feldspar of the enamel with flint, soda, niter, and clay, as is indicated by the ratios given above, it is not possible to obtain enamels of the same physical properties by replacing feldspar with chemically equivalent proportions of other materials. The reason for this is much the same as was noted in discussing the effects of silica from different sources.

Potash feldspar melts at temperatures not far from 1200° C, which is generally well below the temperature of the smelter in melting enamels. In contact with the other materials in an enamel batch it melts at still lower temperatures. Silica in the form of flint, ground quartz, or sand never melts at the smelter temperature, but must be taken into solution by the action of the other materials which are melted in the batch. Therefore the feldspar in the batch becomes an active flux at comparatively low temperatures, thereby accelerating the formation of a homogeneous glass from the components of the batch, while a synthetic mixture of materials giving the same resulting product as the feldspar would contain silica and clay, both of which would retard the melting operation. It would also contain an alkali which melts more readily than the feldspar itself and which is a much more active flux than feldspar. While this vigorous action of the alkali tends to overcome the loss in fusibility of the batch resulting from the extra flint and clay, it at the same time reacts upon those ingredients of the batch which it is desired to keep from solution and decomposition. The result is that, while the fusibility of the enamel is not greatly decreased by substituting other materials for feldspar, the extra time required for melting, together with more vigorous action on the opacifying agents, tends to destroy the opacity of the resulting enamel. Thus, experience has shown that feldspar enamels are more opaque than enamels of the same chemical composition made without feldspar or with a low content of feldspar.

### 3. BORAX

(*a*) PREPARATION.—Anhydrous boric acid ($B_2O_3$), like silica ($SiO_2$), is one of the essential constituents of every enamel, with the possible exception of acid-proof enamels for special purposes. While it is possible to make a silicate containing no $B_2O_3$ of sufficiently low fusing point to use as an enamel, it is very seldom done in enamels for steel and iron because there is no economic gain, and such an enamel is very difficult to apply to these metals.

Many minerals containing boric acid occur in nature, most important of which are the following: Colemanite, $2CaO3B_2O_35H_2O$; borocalcite, $CaO2B_2O_36H_2O$; tincal, $Na_2O2B_2O_310H_2O$; boronatrocalcite, $Na_2O2CaO5B_2O_310H_2O$; boracite, $6MgOMgCl_28B_2O_3$; boric acid, $B_2O_33H_2O$.

Borax, a hydrated borate of sodium corresponding in composition to the mineral tincal, is the source of the $B_2O_3$ most commonly used in enamels. It is obtained by refining the natural mineral, colemanite. The process of manufacture increases the cost of $B_2O_3$ very considerably as compared to the cost if the natural minerals are used. Colemanite can be readily freed from impurities by calcination and screening, and serves as an excellent source of $B_2O_3$ for enamels. In fact it is in many respects much better than borax, and it would seem that the enamelers could advantageously make some arrangement with the producers of borax whereby this mineral might be obtained for their use with a material reduction in cost compared to that of borax.

What has been said of colemanite is also true of boronatrocalcite. While the substitution of either of these minerals for borax necessitates some readjustment of the enamel formula, a considerable saving in cost is possible. This is due not only to the lower cost of the $B_2O_3$, but to the fact that it is possible to produce white enamels with smaller amounts of opacifier (tin-oxide and antimony compounds) when these are used than when borax is used. Borax reduces the effectiveness of the opacifiers by partially taking them into solution during the melting of the enamel, while colemanite and boronatrocalcite are decidedly less active in this respect and do not so seriously affect the opacity of the enamel.

Experiments have been performed to determine the possibility of replacing borax with other minerals containing $B_2O_3$, and the results obtained were entirely satisfactory. White enamels were melted in which colemanite and boronatrocalcite were used to

introduce the $B_2O_3$, and the $Na_2O$ of the borax was replaced with soda ash, the CaO introduced in the colemanite being allowed for by reducing the fluorspar. Enamels of the same ultimate chemical formula were melted side by side, one containing borax, one containing boronatrocalcite, and one containing colemanite. The one containing colemanite was somewhat harder to melt than the others. No difference was noted in the fusibility of those containing borax and boronatrocalcite. When these enamels were applied to iron, the ware made from the colemanite and boronatrocalcite enamels had decidedly the best texture and purest white color.

Colemanite occurs in large quantities in California. Boronatrocalcite occurs in Nevada, Peru, Argentina, Chile, South Africa, and Nova Scotia. Boracite is the chief source of the borax industry in Europe, occurring in considerable quantities near Stassfurt and also near Westergehn (Saxony).

Boracic acid is found in many volcanic regions, the most important deposits being in Tuscany. The crude acid, called Tuscany acid, which is collected in artificial lagoons, is contaminated with sulphate salts, etc., and is colored yellowish brown. It contains about 82.5 per cent boric acid, and can be refined by dissolving in hot water and mixing the solution with freshly ignited powdered charcoal, which removes the coloring matter. The clear solution, upon evaporation, leaves the refined boracic acid of commerce.

Boric acid is not used to any great extent in enamels. It is more expensive as a source of $B_2O_3$ than borax, but it acts similarly to colemanite and boronatrocalcite in not decreasing the efficiency of the opacifying agents. It is also claimed that boric acid is a desirable source of $B_2O_3$ in the production of colored enamels, because the pigments produce cleaner and stronger colors than when borax alone is used.

Regardless of what raw material is used as a source of $B_2O_3$, it is highly essential that it be in a finely divided condition and thoroughly mixed with the batch. There are three forms of borax in use by the enameling trade—powdered, granulated, and crystals. The powdered form is most desirable and will give best results, provided precaution is taken to grind all lumps, and the moisture content is regularly determined. Granulated borax is more commonly used than either of the other forms. It comes in sacks of 100 pounds each, which are convenient to handle.

In general, it is probable that more uniform results can be obtained by its use, because powdered borax always becomes lumpy by absorption of moisture, and these lumps will not always be crushed before mixing in the batch. On the other hand, the crystal borax which comes in large lumps from one-fourth to 1 inch in diameter should never be used. Where borax in this form is used in the enamel, thorough mixing is impossible, and while these lumps melt readily upon being subjected to the heat of the smelter, they immediately take into solution whatever is in immediate contact with them, while other portions of the batch remain unaffected for a long period because of lack of a proper portion of fluxing material.

Borax requires a close watch on its moisture content. It is deliquescent, and its moisture content varies somewhat with the condition of the atmosphere in which it is stored. It is of especial importance that every new consignment of borax received be tested to determine the amount of moisture it contains. The water content of borax is also influenced largely by the condition under which it is precipitated; thus two distinct crystalline forms are obtained of the formulas, $Na_2O,2B_2O_3,10H_2O$ and $Na_2O,2B_2O_3,5H_2O$. The compositions of these two forms of borax are as follows:

| | 1 | 2 |
|---|---|---|
| $Na_2O$ | 16.26 | 22.6 |
| $B_2O_3$ | 36.59 | 47.9 |
| $H_2O$ | 47.15 | 30.8 |

The pentahydrate, containing 5 molecules of water, is found when a saturated solution is allowed to crystallize above 62° C., while that with 10 molecules of water is precipitated from solution below 62° C. Since there is a possibility of these two crystalline forms being present in almost any proportion, it will be readily seen that the enameler has no idea of how much anhydrous borax he is incorporating with his batch unless he knows how much water his material contains. It should be stated, however, that there is little probability of a manufacturer shipping common borax, dekahydrate borax, containing any large amount of the pentahydrate; it would be decidedly to his financial disadvantage to do so, and it is a simple matter to avoid the formation of the pentahydrate when the dekahydrate is being made.

The most simple method of determining the water content of borax is to weigh a definite amount, melt carefully to a glass,

avoiding any loss, and then weigh the glass after cooling in a desiccator. The loss in weight, divided by the original weight and multiplied by 100, gives the percentage of water in the original material.

(*b*) FUNCTION OF BORAX IN ENAMELS. —Borax is used in enamels for its fluxing action, being one of the most active in this respect of all the materials used in the enamel batch. It melts readily and attacks vigorously the other ingredients of the batch, thus accelerating the rate at which the enamel is brought to a uniform molten state. Owing to the high cost of borax and its effect in taking into solution the opacifiers, thereby reducing their efficiency, it is advisable to use as little of it as possible. It is not only valuable as a flux in melting the frit, but it also imparts to the resulting enamel the property of easy fusibility, which is essential. However, this property can be largely controlled by proper adjustment of the ratios between the other ingredients of the batch. Borax also imparts a high luster to enamels, which is more essential in some kinds of ware than in others, but this also can be greatly modified by varying the ratio between the silica and the other ingredients. One of the undesirable properties imparted to enamels by borax is susceptibility to corrosive action. Other things being equal, the solubility of enamels is directly proportional to the $B_2O_3$ content.

Grünwald [1] gives the following table showing the percentage of borax used in raw mixtures of enamels:

| | Per cent |
|---|---|
| Ground for sheet iron | 30–45, usually 35–30 |
| White for sheet iron | 20–34, usually 24–27 |
| Blue for sheet iron | 18–29, usually 28–29 |
| Acid proof for sheet iron | 1[illegible]–24, usually 24–29 |
| White for pottery | 21–41, usually 34–40 |

In American practice the borax content runs from nothing in some acid-proof enamels up to 40 per cent in soft white enamels. The tendency is to use too much borax because it is easy to get an easily fusible enamel of high gloss with a high borax content.

### 4. CRYOLITE

This highly important constituent of enamels is a double fluoride of sodium and aluminum. It functions in the enamel both as a flux and an opacifier. Its chemical formula may be written $Na_3AlF_6$ or $3\,NaF.AlF_3$. It is composed of 32.85 per cent

[1] Grünwald, J., Raw Materials for the Enamel Industry, p. 62, Griffin [illegible]

sodium, 12.85 per cent aluminum, 54.50 per cent fluorine, or 60 per cent sodium fluoride plus 40 per cent aluminum fluoride.

The only known natural deposit of any extent occurs in southern Greenland, from which source all of the natural cryolite in use is obtained. Many brands of artificial cryolite are on the market, some being more nearly pure than that obtained from Greenland. As a rule, the only impurity contained in the natural cryolite is silica, and, if the amount of this is known, the use of cryolite containing it in considerable quantities should cause no serious trouble. It is, however, bad policy to pay the price usually prevailing for cryolite for a brand containing a very large amount of silica, since this can be bought as quartz for very much less than as cryolite. There is no advantage in the natural over the artificial cryolite, provided the chemical composition is the same. However, a few unscrupulous dealers have sold all sorts of concoctions with fantastic names, purporting to be artificial cryolite. Artificial cryolites have been sold containing from 5 to 30 per cent silica. The result is that all artificial cryolite is in bad repute in some quarters.

The mineral, sodium aluminum fluoride, can be made by digesting aluminum hydroxide ($Al_2(OH)_6$) with sodium fluoride, or by precipitating it with common salt when hydrated alumina is dissolved in hydrofluoric acid. The artificial mineral can be made free from impurities, and when so made exhibits all the properties of the natural mineral.

Cryolite melts to a white enamel-like mass at about 1000° C and has a specific gravity of about 2.95. When used in enamel in amounts from 5 to 10 per cent it is an efficient opacifier. It is not good policy to use less than 5 per cent; practically no opacity will be obtained, and its fluxing value in small amounts does not justify its high cost. It is not advisable to use more than 18 per cent, since in larger quantities it tends to destroy the luster of the enamel and to increase its liability to destruction by corrosion.

Much has been written on the subject of fluorides as opacifiers, and many theories have been advanced as to the agent producing this opacity. For discussion on this subject the reader is referred to Staley.[12] All fluorides have the property of imparting some degree of opacity to enamels if the heat treatment is not too severe and the amount of fluoride present is sufficient, but cryolite is the one most generally used and probably the most efficient.

[12] Staley, H. F., B. S., Technologic Paper, No. 142, p. 46.

### 5. FLUORSPAR

Fluorspar ($CaF_2$) or calcium fluoride is composed of 51.3 per cent calcium and 48.7 per cent fluorine. It has a specific gravity of 3.1 to 3.2, and melts at 1400° C. It is an active flux and in large amounts acts as an opacifier. It is distinguished from other lime compounds in that it generally, although not always, reduces the melting point of the enamel.

Lime in some form is desirable in the production of enamels, unless lead is present. Enamels containing no lime are very difficult to smelt and are likely to froth and boil when burned on the ware. A very small amount of lime (1 to 2 per cent) is sufficient to overcome this tendency. When the lime in the batch is low, 4 per cent or less, it is quite unimportant whether it is added as fluorspar or as whiting, but when large amounts are used, fluorspar is the most desirable source because it makes the enamel smelt more easily. The fusibility of the finished enamel will be practically the same if the smelting is thorough, regardless of whether fluorspar or whiting is used.

Fluorspar has a very injurious effect on the color of enamels in which antimony oxide is the opacifier, imparting a bluish-green color. While the color of enamels for steel is not generally of great imprtance, for some purposes a cream or pinkish white is desired rather than blue white. In such cases the fluorspar content of the enamel is of great importance. Enamelers have tried for years to replace tin oxide with antimony oxide and have experienced difficulty in getting the desired color from antimony oxide. The reason for this difficulty has been largely due to the high fluorspar content of the enamels, which gives a correspondingly high fluorine content. The accuracy of this statement can be demonstrated by comparing the color of two enamels containing antimony oxide, using fluorspar in one and in the other replacing the fluorspar by calcium carbonate in the ratio of 100 parts calcium carbonate to 78 parts fluorspar. The one made from calcium carbonate will be cream to yellow, depending on the antimony oxide used, the percentage of calcium and of other ingredients of the batch, while the one made with fluorspar will be blue white to a dirty green.

An enamel containing more than 3 per cent of fluoride will be decidedly weakened in its ability to resist the solvent action of acids, alkalies, or water. This factor is, of course, largely affected by the intensity of the heat treatment during fritting. If the smelting oper-

ation is sufficiently intense to drive off all of the fluorine, then the above statement will not hold, but experience has shown that in the ordinary smelting operation this point is not always reached. The nature of the enamel, its viscosity, and the raw materials used influence this point very materially.

During the smelting the fluorspar decomposes to some extent with liberation of fluorine and combination of the calcium with silica and boric acid. Our knowledge of the reactions in melts as complex as those of enamels is too limited to determine what compounds are actually formed. Such studies as have been made of silicate systems show that the products vary with the heat treatment and the proportions of the different ingredients present. Even where lime and silica only are present, several compounds may be formed. The difficulty of determining what takes place in enamel melts is much greater by reason of the greater number of materials entering into the reactions.

The fact that fluorspar lowers the fusion point of enamels more than an equivalent amount of calcium carbonate does indicate that it is either not completely decomposed or that the fluorine recombines in some form in which it can act as a flux. If the fluorine from the fluorspar is all driven out of the enamel, the compound resulting is probably not materially different from what is obtained when calcium carbonate is used as the source of lime. It is also important to note that the loss of silica from an ordinary enamel would be almost negligible even if all of the fluorine were liberated as $SiF_4$, since an enamel seldom contains more than 8 per cent fluorspar. This gives approximately 4 pounds of fluorine to combine with silicon as follows:

$$SiO_2 + F_4 = {}_4SiF + O_2$$
$$60 + 76 = 104 + 32$$

76 pounds fluorine require 60 pounds silica.

4 pounds fluorine require $\frac{60}{76} = 3.15$ pounds silica.

Thus the silica would be reduced only about 3 per cent in the enamel. While this would be a decided loss in silica, it would hardly be sufficient to make very material difference in the fusibility or in the resistance to corrosion.

It remains, therefore, a matter of conjecture as to the manner in which fluorine is liberated. The tendency of fluorine to combine with silica to form silicon fluoride makes it seem highly probable that the fluorine would come off as $SiF_4$ rather than in

the free state. However, while from a scientific viewpoint this is a very interesting question, the matter in which the enamel manufacturer is chiefly interested is the way in which the fluorides affect his enamel. While the determination of the actual facts would without doubt enable enamelers to more accurately control their products, they can profit greatly by a careful and systematic study of mixtures containing fluorides, even though the exact facts remain unknown.

### 6. BARIUM CARBONATE

Barium carbonate is found in nature as the mineral witherite. It has the chemical formula $BaCO_3$ and belongs to the group known as alkaline earths. The barium carbonate used in enamels is not the natural mineral, but artificially precipitated barium carbonate. It is only within recent years that it has found extensive use in enamels. Its use was brought about by the attempt to eliminate lead from enamels while at the same time maintaining the property of easy fusibility.

Barium carbonate in enamels acts similarly to calcium carbonate in some respects, while in others it resembles lead compounds. It decomposes with great difficulty, and for this reason enamels containing it are difficult to smelt. It is even less active as a flux in the smelter than calcium carbonate, but having been properly smelted it imparts to the enamel the property of easy fusibility, being almost equal to lead oxide in this respect. It is much cheaper than lead oxide and is decidedly less poisonous than lead compounds. It offers a means of producing enamels having the desirable properties of high luster, density, and easy fusibility of lead enamels without the dangers of poisoning attending their use.

In using barium carbonate, care must be taken to obtain a grade free from barium sulphate. Barium sulphate is injurious to enamels, destroying their luster and frequently causing blisters in white enamels.

### 7. ZINC OXIDE

Zinc oxide is closely related to tin oxide in its chemical nature. It is used very extensively in making some types of glazes, notably Bristol glazes for stoneware. In these glazes zinc in connection with alumina is the chief opacifying agent. It is an active flux when used in small amounts, but an excess of it produces infusibility. While it is an efficient opacifier in pure silicate glazes, it has practically no opacifying power when fritted in borosilicate enamels.

It is used quite extensively in making enamels, chiefly for its fluxing power and its property of increasing the stability of enamels against corrosion. It is very similar to barium in the effect it has on enamels. It is less active than barium in reducing the melting point, but it produces somewhat more stable enamels. Used in small amounts it gives enamels with high luster, but excess destroys the luster. It is bad practice to add raw zinc oxide in the mill. It is not efficient as an opacifier when thus used, and it destroys the luster and imparts a bad color to the enamel.

### 8. SODIUM AND POTASSIUM SALTS

Soda ash is the form in which soda is commonly introduced into enamels, except that brought in by borax and cryolite. It is anhydrous sodium carbonate ($Na_2CO_3$), composed of 58.5 per cent $Na_2O$ and 41.5 per cent $CO_2$, and is to be distinguished from the crystalline or hydrated sodium carbonate ($Na_2CO_3 10H_2O$). The water in the latter material may be expelled by heating to 100° C. The anhydrous sodium carbonate is also known as 58 per cent soda ash. It is a very active flux in enamels.

All enamels contain some sodium oxide, derived chiefly from borax, cryolite, and soda ash. The fusibility and liability to corrosion are increased with increase of $Na_2O$ and $K_2O$. These two oxides seem to be interchangeable in enamels without any very material difference being noted in the results. There is an opinion prevailing that potash gives a little more luster and strength to enamels than soda, but no data is available to substantiate this claim. The carbonate of potash has the disadvantage of being more expensive than soda, and because of its hygroscopic nature it is troublesome to handle. It is therefore seldom used in enamels.

Most enamels contain some oxidizing agent in the form of either potassium or sodium nitrate. Sodium nitrate is generally used because it is the cheapest. Only a small amount of nitrate is necessary, 2 to 4 per cent being sufficient to maintain oxidizing conditions in most smelting operations. It is highly important that sufficient niter be present to prevent reduction of any easily reducible compound in the batch, especially lead or antimony compounds. The color of the resulting enamel is very materially affected by slight reduction, which may be caused by a smoky flame or by carbonaceous compounds incorporated in the batch. It is of especial importance that enamels containing antimony oxide have sufficient oxidizing agent. Reduction of such an

enamel not only causes the antimony to go into solution, thereby losing its opacifying power, but it destroys the color of the enamel. Commercial materials always contain some impurities, and there is generally a sufficient amount of iron compounds in the materials to affect the color. This effect will be much more pronounced if the batch is not kept oxidizing during smelting. When the batch is thoroughly oxidized, as much as 1 per cent of red oxide of iron can be incorporated in a white enamel without any serious damage to the color, but if the batch is reduced in smelting the color will be very dark and the enamel therefore unsuitable.

For the production of some colored enamels, reducing conditions are desirable, in which case the niter should be left out. Black and dark-blue enamels may be mentioned as cases in point. While these colors can be produced under oxidizing conditions, they will be produced more cheaply and easily under reducing conditions.

The amount of niter in the batch has also an effect on the melting. Enamel without any niter melts with much less frothing than that containing it in sufficient amount to maintain oxidizing conditions. Excess of niter should be avoided, therefore, because it is expensive, because no benefit is derived from using it as a flux rather than some cheaper form of alkali, and because it increases the difficulty of smelting.

### 9. COMPOUNDS OF ANTIMONY

Antimony, either as the oxide or as some other compound, is one of the principal opacifiers used in making white enamels. In normal times these compounds are much cheaper than tin oxide and when properly used are effective as opacifiers. There are many difficulties attending the use of antimony compounds in enamels, and unless all conditions are right poor results are likely to be obtained.

When heated in the absence of strong acids with bases like sodium, potassium, barium, or lead, antimony oxide functions as a weak acid with formations of antimonates. It is capable of combining with the bases in many different proportions. It is quite a simple matter to form glasses varying from $3RO{\cdot}Sb_2O_3$ to $RO{\cdot}3Sb_2O_3$ by merely mixing the materials and heating. The mixtures melt readily to liquids and can be poured into water and granulated, being quite insoluble in water. They vary in color from a cream to dirty brown, but seldom approach white.

Antimony oxide occurs in three forms: as trioxide, $Sb_2O_3$; tetroxide, $Sb_2O_4$; or pentoxide $Sb_2O_5$. The trioxide and pent-

oxide are of a yellow color, while the tetroxide is white. When $Sb_2O_3$ is heated to 275° C, it is converted to $Sb_2O_5$. This, upon being heated to 300° C, is in turn converted to tetroxide, which is the most stable form of the oxide.

Antimony compounds have found extensive uses as opacifier because of certain advantages they posses over the oxide itself One of these is that the combined antimony, if properly prepared, can be incorporated in ordinary enamels with less modifications of the batch than is necessary when the oxide itself is used. As mentioned before, one of the principal difficulties encountered in using antimony oxide is the control of the color, the antimony affecting the color by combining with different bases forming dark-colored compounds. When the oxide itself is added in the smelter, it combines quite readily, but when it is added in the form of antimonate of some base, it seems to be quite stable, and thus not only has a high efficiency as an opacifying agent but also combines to a smaller extent with formation of undesirable colored compounds.

The results obtainable by using antimony oxide direct depend largely on the quality of the oxide used. The oxide on the market in normal times varies in color from a pure clean white down through a pleasing cream color to a dirty gray. The apparent density of the oxide also varies greatly, depending upon the method of preparation. That prepared by wet chemical processes has a high density—that is, apparent specific gravity—and is generally very clean and white. That deposited from vapor is a light fluffy powder. Better results are obtained with the dense clean white oxide than with the other forms.

Several factors affect the quality of the enamel, and these must be carefully adjusted. If a cream color is desired, the fluorspar content of the enamel must not run above 4 per cent of the raw batch when the antimony oxide is used. Enamels containing fluorspar and antimony oxide have a blue-green color. This color can be largely corrected by additions of cryolite, which acts as an opacifier and masks the blue-green color of the fluorspar-antimony compound. Other fluorides, like sodium fluoride and aluminium fluoride, are not detrimental to the color. Lime in the form of $CaCO_3$ used in connection with $Sb_2O_3$ gives good cream colors, but the enamel is more difficult to smelt The use of sufficient oxidizing agent, niter, is a very important factor in obtaining a good white color.

## 10. EFFECT OF OTHER CONSTITUENTS OF ENAMEL ON THE COLOR PRODUCED BY ANTIMONY OXIDE

As a basis for this study, the following formula, X, was used:

| | |
|---|---|
| Potash feldspar | 40 |
| Borax | 24 |
| Soda ash | 6 |
| Sodium nitrate | 7 |
| Fluorspar | 3 |
| Barium carbonate | 5 |
| Zinc oxide | 10 |
| Antimony oxide | 6 |

Three different samples of antimony oxide were taken, as follows:

No. 1. Domestic oxide of a dirty gray color, which gave a muddy greenish-yellow color in enamel X.

No. 2. French oxide of a rather strong yellowish color, but which gave fair-colored enamels, tending to a rather strong cream.

No. 3. Best French oxide obtainable, which was of a pure white color and gave a good white enamel.

Samples of each oxide were thoroughly wetted with concentrated nitric acid and immediately roasted to dryness over a hot plate at 110° C, roasting being continued until all fumes ceased to come off and the powder was fine and of uniform color. This roasting converted all of the oxides to a dirty gray color, and when they were mixed in enamel and melted the result was a dirty appearing enamel.

The same oxides were boiled for 30 minutes in concentrated nitric acid. The solution was diluted and filtered and the precipitate was washed free from acid, then calcined at 1000° C. This treatment converted all samples to a clean, cream color, and these, when used in enamel X, gave a clean, cream-colored enamel.

In order to determine the effect of flourspar in antimony enamels, 50 g batches of the above mixture, leaving out the fluorspar, were weighed up and thoroughly mixed by grinding in a ball mill. Fluorspar was added, as follows:

(*a*) X with 4 per cent $CaF_2$
(*b*) X with 5 per cent $CaF_2$
(*c*) X with 6 per cent $CaF_2$
(*d*) X with 7 per cent $CaF_2$
(*e*) X with 8 per cent $CaF_2$
(*f*) X with 9 per cent $CaF_2$

These mixtures were placed in crucibles in a furnace and all melted at once, the enamel poured out, and colors compared. The mixture with 4 per cent $CaF_2$ gives a fair color with a slight bluish tinge; 5 per cent $CaF_2$ gives a blue tinge; 6 per cent $CaF_2$, a decided

blue; and 8 per cent, more color. The color is distinctly bad with 6 per cent fluorspar.

Lime was then introduced in the enamel in other forms:

(*g*) X with 0 $CaF_2$ + 3 per cent $CaCO_3$
(*h*) X with 0 $CaF_2$ + 5 per cent $CaCO_3$
(*i*) X with 0 $CaF_2$ + 7 per cent $CaCO_3$
(*j*) X with 0 $CaF_2$ + 9 per cent $CaCO_3$
(*k*) X with 0 $CaF_2$ + 3 per cent $Ca(OH)_2$
(*l*) X with 0 $CaF_2$ + 5 per cent $Ca(OH)_2$
(*m*) X with 0 $CaF_2$ + 7 per cent $Ca(OH)_2$
(*n*) X with 0 $CaF_2$ + 9 per cent $Ca(OH)_2$

None of these exhibit the blue color, but the opacity is decidedly less with $CaCO_3$ as the source of lime, and the enamel is more difficult to smelt. The use of $Ca(OH)_2$ is unsatisfactory as a source of lime, because the enamel froths when melting and is melted to a dense glass only with the greatest difficulty.

Enamels were melted, using different fluorides, as follows:

(*q*) X – fluorspar + 3 per cent BaF
(*r*) X – fluorspar + 8 per cent BaF
(*s*) X – fluorspar + 3 per cent NaF
(*t*) X – fluorspar + 8 per cent NaF
(*u*) X – fluorspar + 3 per cent cryolite
(*v*) X – fluorspar + 8 per cent cryolite
(*x*) X – fluorspar + 6 per cent $CaCO_3$ + 6 per cent cryolite
(*y*) X – fluorspar + 8 per cent $CaF_2$ + 10 per cent cryolite

None of these enamels exhibited the blue color obtained when fluorspar alone is used. These results seem to show that fluorspar, when melted with antimony oxide in enamels of this type is responsible for the objectionable blue color.[13]

Leukonin is an antimony compound, sodium metantimonate ($Na_2OSb_2O_5$), made by roasting antimony oxide with soda compounds the excess of which can be leached out with water, leaving sodium antimonate. This material, as sold, contains from 85 to 97 per cent $Na_2OSb_2O_5$ and other substances as impurities. Leukonin is used successfully in enamels.

## IV. PREPARATION OF ENAMELS

### 1. MIXING THE RAW MATERIALS

General practice in mixing the raw materials consists in weighing the batch, which generally approximates 500 pounds, into a box

[13] Cf. Staley, H. F., Trans. Am. Ceram. Soc., 17, p. 173.

and then turning the mixture over a few times with a hoe or shovel. In the case of colored enamels it is considered mixed when the coloring oxide is uniformly distributed, imparting a uniform gray color to the batch. In white enamels the practice is to turn the mixture a certain number of times, which is considered to be sufficient. Here is one of the places where enamelers can improve their practice and raise the standard of their ware by doing away with slipshod methods and resorting to more thorough, exact, and economical methods. Rotating drums and other forms of mixing machines give much more satisfactory results.

Every enameler, and even the uneducated laborer who has worked around the smelter, has observed that the enamel smelts more quickly when most thoroughly mixed. This is simply the practical application of the well-known scientific principle that the speed of chemical reactions is directly proportional to the area of surface of contact between the reacting substances. If a fire brick were crushed to a powder and mixed into the batch it would go into solution in the melt and disappear with the other ingredients of the batch, while that same brick when laid in the wall of the smelter will stand for months without being eaten away. This same principle applies to all the refractory ingredients of the batch. A large piece of flint stone will go through a melt and come out with only the sharp edges eaten off. The length of time required for smelting the enamel depends directly upon the fineness of the raw material, especially flint and feldspar, and upon the thoroughness with which they are mixed. It follows, then, that better mixing of the raw materials means less labor, less fuel, less time of smelting, and less wear and tear on the smelter.

It is not only from an economic standpoint that thorough mixing is advisable. The quality of the white enamels is inversely proportional to the length of time spent in producing a thorough melt. Long smelting results in a considerable reduction in opacity. Fine grinding and thorough mixing insures a uniform fusion product in the shortest possible time and hence minimum solution of opacifying agents and minimum reduction in opacity.

### 2. MELTING

In the smelter the enamel mixture is melted and fined until no lumps of unfused or undissolved material can be detected in a string of the glass drawn from the melt. The melting process begins with the fusion of the least refractory ingredients or fluxes — borax, soda ash, etc. — at relatively low temperatures. The liquid

attacks the more refractory substances both by solution and by chemical reaction. The formation of eutectics between the raw materials and the compounds resulting from chemical reaction facilitates the melting process.

If the smelting process is continued for a sufficient length of time a perfectly homogeneous glass in which all constituents would be in equilibrium would result. Such a condition is not obtainable, especially in white enamels. The melting should proceed only to the point where a stable borosilicate glass is formed, in which the opacifying agents, fluorides, tin oxide, and antimony compounds are carried in suspension. Longer smelting results in a considerable solution of these materials, as well as decomposition of the fluorides and consequent reduction in the opacity of the enamel. No opacity is obtained from tin or antimony oxides after they are once taken into solution. Quick smelting is therefore to be desired, and this again calls attention to the value of fine grinding and thorough mixture of the raw materials.

An interesting investigation of the effect of time of smelting on the nature of enamel frits has been made by Poste and Rice.[14] As a result of the studies they have drawn the following conclusions:

1. Fluorine from fluorspar is all driven out of the enamel in the very early stages of smelting.

Strictly speaking, this applies especially to the particular enamel with which Mr. Poste is dealing, but it, no doubt, applies equally well to many other enamels. On the other hand, there is no doubt that in some enamels the fluorine will be retained after prolonged heat treatment.

2. The fusibility of the frit decreases as the time of fritting is increased.

3. Alkalies and boric acid decreases and silica increases as the time of fritting is increased.

This condition is brought about by volatilization of alkalies and boric acid. The curves obtained indicate that lime and aluminia do not change. It would seem that these should vary the same as silica, in view of the fact that neither volatilizes to any extent.

4. The fusion range is greatest just at the point where the frit would normally be drawn from the smelter.

5. The ability of the frit to resist solutions increases as the length of time in the smelter is increased.

[14] Poste, L. P. and Rice, B. A., The Effect of the Degree of Smelting Upon the Properties of Enamel Frits, Jour. Am. Ceram. Soc., 1, p. 221

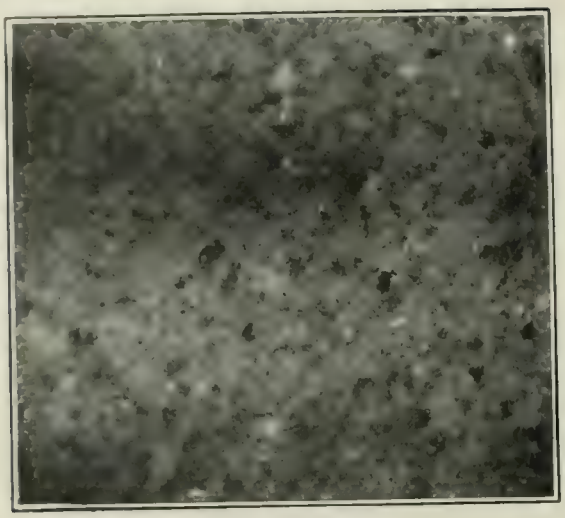

FIG. 1.—*Sample A–1. Underfired enamel, oblique illumination.* × 75

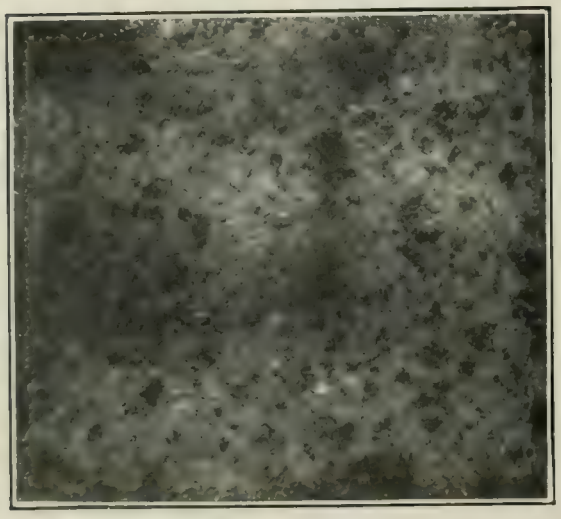

FIG. 2.—*Sample A–2. Properly fired enamel, oblique illumination.* × 75

FIG. 3.—*Sample A–3. Overfired enamel, oblique illumination.* × 75

The same investigators used a relatively soft formula, which is in commercial use, in making a series of trial cups which were burned under varying conditions. The first piece, designated as A–1, was underburned, but to a degree which would not carry it far beyond a commercial possibility. The second, A–2, was given as near the proper burn as possible, and the third, A–3, was somewhat overburned. The resulting pieces were examined under the microscope with oblique illumination and a magnification of about 75 diameters at the plate of the camera.

SAMPLE A–1.—A medium blue enamel with fair gloss, the surface being slightly rough to the touch. Under the microscope this enamel shows an indefinite field of unfused material and minute bubbles, with practically no large bubbles.

SAMPLE A–2.—The enamel is about the same in color as A–1, but has a much better gloss and is smooth to the touch. There is no surface pitting. The microphotograph shows a reasonably uniform field similar to that obtained from A–1, and in addition a noticeable distribution of large bubbles on a background containing unfused material and fine bubbles.

SAMPLE A–3.—The color of the enamel is much darker than A–1 and A–2. The gloss is very good, but there is a tendency for surface pitting. On magnification there is found to be a dark-blue background of homogeneous glass showing no unfused material. In the foreground is a very even distribution of large, well-formed bubbles.

### 3. TEMPERING ENAMEL SLIPS

In preparing enamel slips for application to the ware the frit is ground wet and contains 5 to 10 per cent (by weight) of plastic clay. To increase the viscosity of the slip and aid in holding the enamel in suspension, a flocculating agent is added. In white or cover enamels magnesium sulphate is generally used for this purpose. In ground coats borax is almost universally employed, since nearly all other salts which have a similar effect on the slip are likely to cause rusting of the steel during the drying of the ware.

Prior to the outbreak of the war the Vallender clay from Germany was almost exclusively used by enamelers in preparing their slips. This is a very clean and highly plastic clay. The necessity of finding a substitute for this material has brought on the market a number of American clays of varied quality. It was generally considered by enamelers that none of these satisfactorily replaced the German clay.

An investigation of the properties of several clays for enameling purposes was carried out by the writer[15] with the object of finding a clay or a mixture of clays, American, if possible, which could be satisfactorily used to float enamels, preventing them from settling to the bottom of the dipping tub and permitting tempering to a proper consistency to obtain a uniform coating of desired thickness on the surface of the ware. It was thought that ball clays were most likely to give the desired result, but the Florida clay was included since it had been used for this purpose on different occasions. The clays selected were:

No. 1. Kentucky ball clay.
No. 2. Tennessee ball clay, J. K. Porter No. 11.
No. 3. German Vallender clay.
No. 4. Georgia clay.
No. 5. Florida clay.
No. 6. English ball clay, M. & M.
No. 7. A clay supplied to the trade, resembling Florida clay, included in part of the tests.

A series of experiments was made, treating the clays with electrolytes, to determine their properties as compared with the Vallender clay. In all the clays the results showed some similarity to the German clay, but on the whole they may be placed in the order: Nos. 2, 5, 1 and 4, 6, as regards their resemblance to No. 3.

Experiments were next made to determine how the clays would act when used as the agent for floating the enamels.

There are five factors which greatly influence the floating of frits in enamel or glaze slips: (1) Size of grain of the frit; (2) specific gravity of the frit; (3) concentration of frit in the slip; (4) viscosity of the floating medium; (5) amount of the floating medium.

1. Fine grinding makes the frit more easy to float, but enamelers dare not grind too finely, because of difficulty in getting a uniform coating on the ware. Ground coat enamels especially must be coarse, not finer than 100 mesh, and, better, 80 mesh.

2. Lead enamels would, of course, be more difficult to float than lighter ones, but lead is seldom used in enamels for sheet iron. However, all frits are relatively high in specific gravity as compared with clays and therefore settle more readily.

3. Settling is easily prevented by making the slip thick, approaching a paste, but in order to apply them by dipping or spraying, slips must be sufficiently fluid to flow. With such a

[15] Shaw, J. B., American Clays for Floating Enamels, Trans. Am. Ceram. Soc., 19; 1917.

consistency heavier substances will settle unless a floating agent is used.

4. Viscosity has been described as the friction between two liquids flowing in contact with each other, or between a liquid and a solid moving in it; in other words, resistance to flow. The efficiency of a floating medium in preventing the settling of heavier particles, therefore, depends upon its viscosity or resistance to the motion of particles passing through it. The floating medium in the case of enamels is not to be considered as the water, but as the clay substance in suspension in water.

High viscosity is also required in enamel slips to prevent them from flowing down the sides and into the corners of the ware after dipping. A steel body, being nonabsorbent, offers a different problem from that of a porous body dipped in a glaze slip. The absorption by the porous body prevents the flowing of the glaze, but the enamel slip must stay in place by virtue of its viscosity, although it is possible that surface tension also plays an important rôle here.

5. It is evident that a sufficient amount of the floating medium to prevent settling can readily be added, but other considerations limit the amount of clay which can be used with any glaze or enamel, about 10 per cent being the maximum permissible in the latter. The efficiency of the clay as a floating agent is therefore highly important, especially in enamels where the frit is of higher specific gravity and more coarsely ground than in glazes or engobes, and where the amount of clay used is necessarily small.

(*a*) Settling of the Enamel.—The relative amount of settling of the enamel when the several clays with different flocculating agents as the floating medium were used was determined as follows: The frit was ground dry to pass an 80-mesh screen, and the slip was prepared by weighing out frit and clay and adding the required amount of water and electrolyte. The slip was shaken for two hours.

In a second series of tests the slips were made up without other flocculating agents, ground wet to pass an 80-mesh sieve, and, after standing for 18 hours, were tempered with water and the electrolyte. They were then shaken by hand for 1 minute.

After shaking the slip, in both cases, it was allowed to stand for 18 hours. The volume of clear water on top was measured and this was decanted off. The weight and volume of the remaining slip was then determined and the upper half of this

decanted off. The weight and volume of the lower half of the slip was determined. From these measurements the amount of settling of the enamel was indicated by the amount of clear water over the slip after standing, and by the relative specific gravities of the original slip, of the residue after decanting off the clear water from the tubes after standing 18 hours, and of the lower half of this residue. The less the increase in specific gravity from that of the original slip to that of the lower portion in the tube after standing, the less the settling of the enamel.

The results showed the Tennessee ball clay (No. 2) to most nearly resemble the Vallender clay in ability to keep the enamel in suspension. The kaolins (Florida and Georgia) gave surprisingly good results in this respect.

It is to be noted that the conditions in this experiment do not conform exactly to those in the dipping tubs in enameling wo k where the stirring of the slip has the effect of washing out the heavier particles and facilitates sedimentation as soon as stirring ceases. Occasional stirring of the top part of the slip causes the frit to settle out and leaves the clay in suspension.

(*b*) VISCOSITY MEASUREMENTS.—In view of the importance of the degree of viscosity in enamel slips, considerable attention was given to the measurement of this in testing the floating properties of the clays. After trying several types of apparatus a viscosimeter was devised which gave excellent results in this work, and it is thought that a similar one might be used to advantage by enamelers in maintaining uniform consistency in their slips. It might also be of value in the preparation of glazes and engobes.

The apparatus [16] consists of a brass cylinder, 1½ inches in diameter, provided at the bottom with two efflux tubes 1 inch long and of three thirty-seconds and five thirty-seconds inch bore, respectively. These are closed by caps, which are leld in place by a spring. Graduated tubes are placed under each efflux tube to measure the amounts of slip which flow from these after releasing the spring holding the caps. The viscosity determination is based on the following considerations:

The quantity of liquid flowing through a short tube or orifice is represented by

$$Q = KA\sqrt{2gh}$$

where $K$ is a constant for a given tube and liquid, its value depending upon the frictional resistance to flow, $A$ is the area

[16] Trans. Am. Ceram. Soc., 19, p. 349.

of the tube, and $gh$ represents the velocity of flow. In this apparatus the flow through the two tubes, $a$ and $b$, is represented by

$$Q_a = K_a A_a \sqrt{2\,gh} \text{ and } Q_b = K_a A_b \sqrt{2\,gh}.$$

The ratio of flow from the two tubes is

$$\frac{Q_a}{Q_b} = \frac{K_a}{K_b} \cdot \frac{A_a}{A_b} \cdot \frac{\sqrt{2\,gh}}{\sqrt{2\,gh}}.$$

Hence

$$\frac{K_a}{K_b} = \frac{Q_a}{Q_b} \cdot \frac{A_b}{A_a} = KX = \text{viscosity}.$$

In the case of water

$$Q_a = 45 \text{ cc}, Q_b = 15 \text{ cc},$$

and

$$\frac{K_a}{K_b} = \frac{45}{15}, \frac{A_b}{A_a} = 3\frac{A_b}{A_a}.$$

Since $\frac{A_b}{A_a}$ is constant, the values for relative viscosity with this apparatus may be expressed as $\frac{Q_a}{Q_b}$.

It is the general practice to refer viscosities to that of water as unity, but for comparative purposes it seems satisfactory to express the values as given by the instrument itself, whereby water gives a viscosity value of 3.

The viscosities of enamel slips made up with the different clays and with various electrolytes, and using different water contents, are shown in the curves of Figs. 4 to 6. The more rapid the increase in viscosity with increase in specific gravity of the slip, the better the action of the clay as a floating agent.

In Fig. 4 it is noted that the Tennessee ball clay is fully as good in this respect as the Vallender clay, while the Kentucky ball clay and a mixture of Tennessee and Florida clays are good, the latter being much the better.

In Fig. 5 the Vallender clay appears greatly superior to the others. The use of borax as the electrolyte conforms to general factory practice, and it is in enamels tempered with borax that the greatest difficulty in floating occurs.

A comparison of the curves in Figs. 4 and 5 shows that high viscosities are obtainable with slips of much lower weight per 100 cc when magnesium sulphate is used than when borax is used. A heavy slip is difficult to distribute uniformly on the ware and tends to flow down the vertical surfaces because of its high specific gravity, which tends to overcome the viscosity.

The enameler attempts to get the proper degree of viscosity with a slip of certain specific gravity and learns by practice to recognize the proper conditions. A viscosity value as low as 4.5 is permissible for enamel slips, if the weight per 100 cc does not much exceed 150 g. The low viscosities obtainable, when no flocculating agent is used, even with slips of high specific gravity, are shown in Fig. 6.

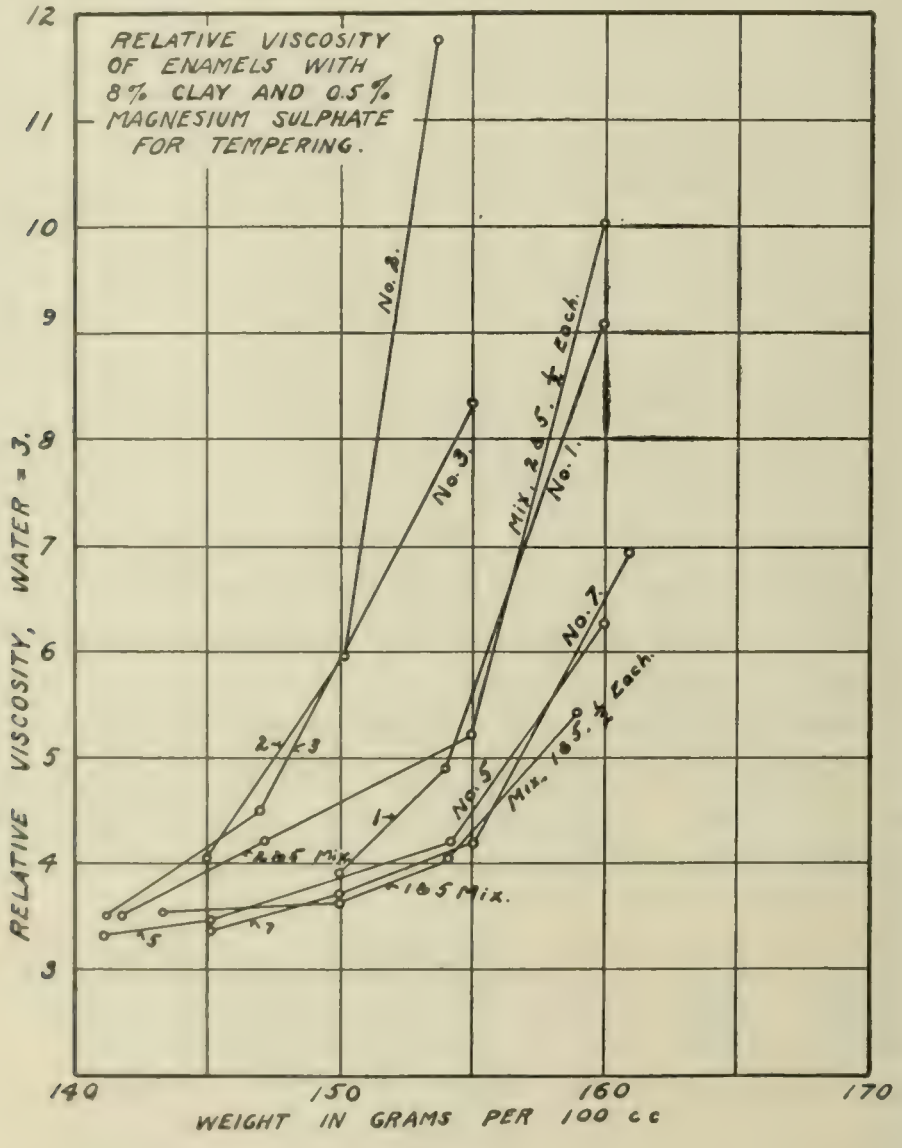


FIG. 4

Comparison of the results with the various slips and in the various tests shows little relative change in the position of the clays, but a decided difference in the effects of the various flocculating agents. The Vallender clay is apparently decidedly superior to the others; the Tennessee ball clay comes next, and is in some respects better than the Vallender. The Florida clay also shows good results.

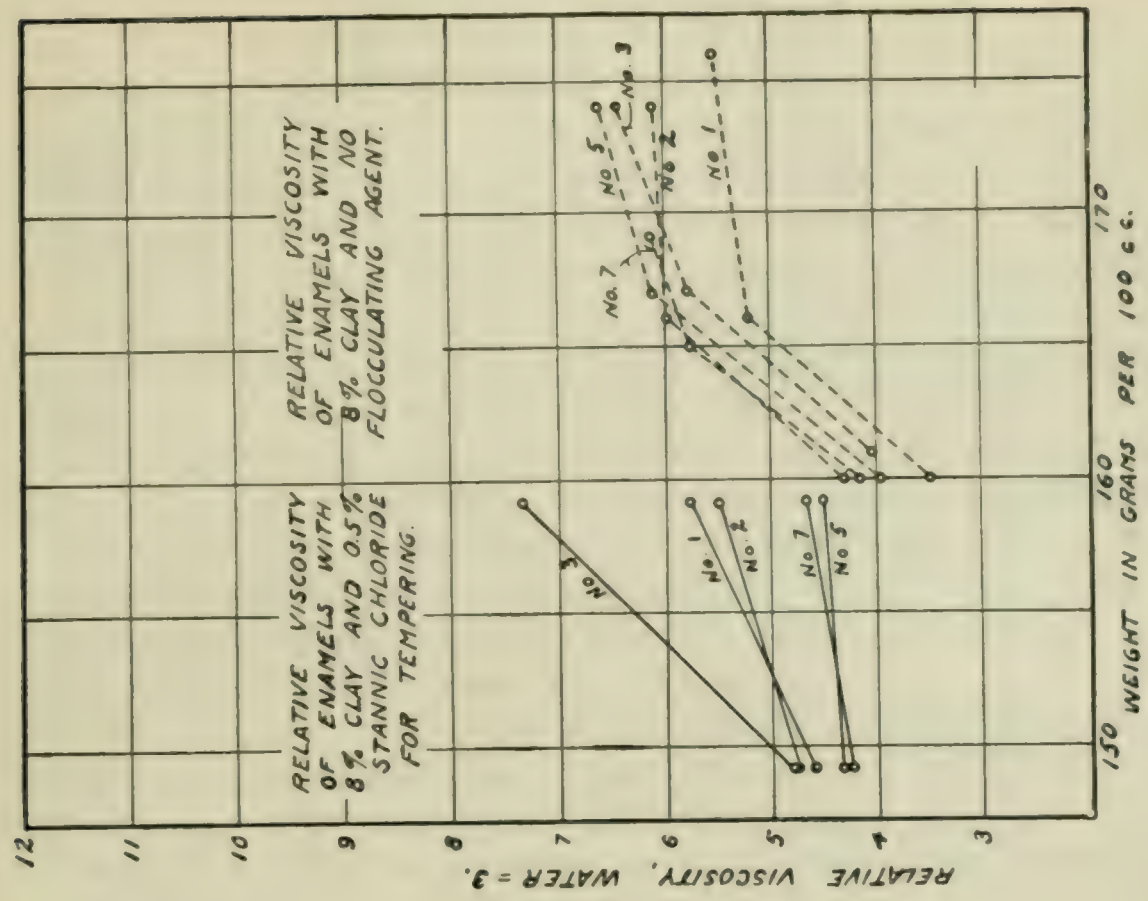
RELATIVE VISCOSITY OF ENAMELS WITH 8% CLAY AND 0.5% STANNIC CHLORIDE FOR TEMPERING.
RELATIVE VISCOSITY OF ENAMELS WITH 8% CLAY AND NO FLOCCULATING AGENT.
No. 1
No. 2
No. 3
No. 5
No. 7
RELATIVE VISCOSITY, WATER = 3.
WEIGHT IN GRAMS PER 100 c.c.

FIG. 6

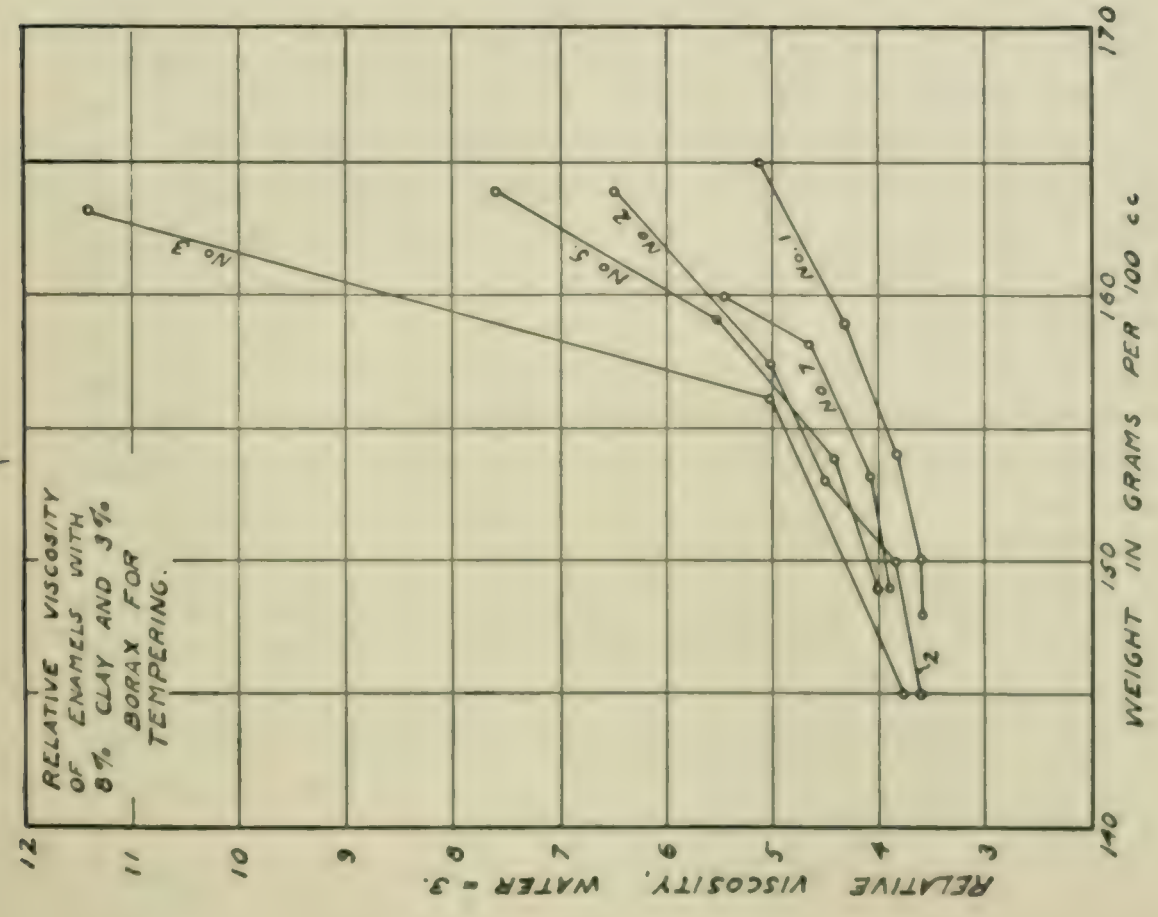
RELATIVE VISCOSITY OF ENAMELS WITH 8% CLAY AND 3% BORAX FOR TEMPERING.
No. 1
No. 2
No. 3
No. 5
No. 7
RELATIVE VISCOSITY, WATER = 3.
WEIGHT IN GRAMS PER 100 c.c.

FIG. 5

## V. ENAMELING PROCESS

### 1. APPLICATION OF THE ENAMEL

There is no more vitally important operation in the entire process of enameling than the application of the first coat of enamel. A piece of ware which has passed through the operations of forming and cleaning has acquired considerable value to the manufacturer on account of the labor expended upon it. In the application of the ground coat it is possible to enhance this value or to destroy it, or, still worse, to so treat it that it will pass through the succeeding operations and still be worthless as a finished piece of ware. Given a good ground coat, properly applied and burned, the finishing of the ware is simple. The very best ground coat improperly applied or burned can give only a poor piece of ware, regardless of what its previous cost or future treatment may be. Every possible precaution should therefore be taken to insure a suitable coating on the steel.

Four different methods are used for applying the enamel to the steel—slushing, draining, spraying, and dusting. The choice of method depends upon the size and shape of the ware and the nature of the enamel. The chief factor to be considered in the application of the enamel is to obtain a coating of uniform and sufficient thickness on the surface of the ware. If a thin and uniform coating is not obtained, the enamel will burn off the portions where it is too thin and will not be sufficiently burned where it is thick. Either of these defects will cause the finished ware to be defective. The method best suited to produce this result, with due consideration to the cost of the operation, is the one generally used.

(*a*) SLUSHING.—By far the greatest proportion of enameled ware is slushed, especially in the case of all light wares and such as can be easily shaken to distribute the enamel uniformly. The operation consists in dipping the piece of ware into the enamel slip, removing it and shaking it in such a way as to leave a thin and uniform coating over the entire surface of the metal. There are two factors of vital importance in securing proper results by this method—the consistency of the enamel slip and the skill of the operator. The consistency of slip for slushing is such as is termed "short," that is, it has a high viscosity and will not run down or drain off from vertical surfaces after dipping.

To the novice it would seem a simple matter to dip a piece of steel into a tub of slip, shake off a little, and obtain a nicely coated

piece of ware. As a matter of fact, considerable practice is required to acquire skill sufficient to slush even simple shapes uniformly, while extensive training and a very high degree of skill is required in the handling of complicated shapes.

(*b*) DRAINING.—This method is frequently applied to perfectly flat ware, such as signs, and to simple shapes. The piece of ware is dipped in the slip and is then set on edge to allow the excess to run off at the bottom. The consistency of the slip, which is very different from that used in slushing, is the principal factor in the success of this operation. In this case the viscosity is much lower, so that the slip will flow down the vertical surface, but at the same time its consistency must be such that it will form a good coating and adhere to the ware after the excess drains off. It must also be sufficiently viscous to keep the enamel in suspension and not allow it to settle onto the bottom of the tank.

(*c*) SPRAYING.—For applying enamel to complex shapes and heavy ware, spraying is frequently resorted to. It is too expensive to use on the ordinary grades of ware, but for special shapes with many corners and sharp angles, or any piece of ware which can not be slushed uniformly, spraying is the best method of coating. It is wasteful of material and requires skill to obtain good results, but if proper care is used any piece of ware can be very uniformly coated by spraying. The piece may be placed on a whirling rack and turned while the spray is being applied.

The consistency of the enamel is highly important again in this case. The enamel must be ground sufficiently fine to prevent stopping the nozzle of the sprayer, but for best results it must not be too finely ground. Its viscosity must be high to prevent flowing. Since the distribution of the slip over the surface is accomplished in this case by the movement of the spray and not by shaking the piece, it is possible to work with a higher viscosity than in slushing.

(*d*) DUSTING.—This method of application is very common in cast-iron work, but in steelwork it is used only on heavy wares, such as condensers for chemical works, etc. It has a decided advantage in the production of acid-resisting wares, because no raw materials are added to the frit, whereas when any of the other methods of application are used, it is necessary to add some raw clay and soluble salts to the frit in order to get a slip of the proper consistency. These raw materials are invariably decidedly injurious to the enamel, especially where resistance to chemical

corrosion is desired. While an enamel is a glassy coating, it is far from being a solid glass; and the more raw material added in grinding the frit the further is the finished enamel removed from this condition, since these raw materials are only to a very slight extent combined with the frit during the brief burning operation. Because of this fact the dusting method is decidedly the best to use for making enameled ware to resist chemical corrosion.

In carrying out this process, the ground coat, as well as cover coat, is frequently dusted on. The metal is wiped with a wet sponge or cloth, and the powder dusted on while the metal is still wet. Sometimes an adhesive agent is added to prevent the enamel from falling off when dry.

The methods used for cover enamels are the same as those used for ground coats. The quality of workmanship in applying cover coats is far less important than in applying ground coats. If a piece of ware is perfectly coated with the ground coat, the cover coat may be quite imperfectly applied and still give good results. Of course there are limits to this, and the more uniformly the enamel is applied the better it will be. It should be said, further, that best results are always obtained with thin enamels. Barring the properties of whiteness and opacity, the excellence of enamels is inversely proportional to their thickness. This is especially true of the ability of the ware to withstand bending and abrasion. In view of these facts the aim should always be to keep the enamel as thin as possible, while at the same time obtaining the desired opacity and color.

### 2. DRYING

Ground-coat enamels should be dried as rapidly as possible to prevent rusting of the steel. This will be controlled to some extent by the flocculating agents used in the slip, but rapid drying is the best practice in any case. If an alkaline flocculating agent is used for tempering the ground coat, it can be dried in the open air without serious rusting; but if chlorides or sulphates are used, rusting is almost sure to result even with rapid drying. This rust may or may not be visible after the ware is dry, but it is quite sure to make its appearance, when the ground coat is burned, in the form of spots where the iron oxide has reacted with the enamel to such an extent as to form a spot-like iron scale. When these spots are formed, it is practically impossible to cover them with cover enamel. They will show in the finished ware either as dark spots or as pits in the surface. While proper drying of the ground coat can not entirely prevent this trouble in an improperly tempered

enamel, it will always reduce the trouble, and when the ware is not dried rapidly the trouble is likely to come even in the best tempered enamel.

The rate of drying of cover enamels is of less importance than in drying ground coats. However, rapid drying is here again desirable. One of the chief reasons for this, especially in white enamel, is the fact that dirt in the form of factory dust sticks to the ware while wet, and therefore rapid drying of the white enamel makes for pure white ware. Another point in favor of rapid drying of finished ware is the need of space for storing the ware. After the enamel is dry the ware can be handled and stored in much less space than when wet, and in making some classes of wares, such as cooking utensils, the problem of finding room for storing sufficient ware to keep the furnaces going is sometimes troublesome. There are two common defects caused by improper drying. Water streaking, caused by moisture from drying ware condensing on the cold surface of wet ware and running down vertical surfaces in streaks, can be avoided by proper circulation of air in the dryer. When ware is dried too rapidly the enamel will crawl. This is caused by the formation of shrinkage cracks due to driving off the moisture from the clay too rapidly. These cracks do not show in the dry ware, but when it is burned the enamel crawls and collects in beads. This defect will be caused when a piece of wet ware is set on a hot piece of metal or when the drying is very sudden. The same defect may result from rough handling of the dry ware, a sudden sharp blow breaking the bond between the dry enamel and steel, which results in crawling.

### 3. BURNING ENAMELS

(*a*) General Description.—Muffle furnaces are almost invariably used for burning light wares and especially white ware. For burning heavy steel wares open furnaces are used.

The general practice is to have a burner and a helper working on a furnace. The helper will acquire skill as a burner after he has worked on the furnace a few months under the tutoring of the experienced burner. The importance of this period of apprenticeship is generally overestimated. One of the best burners the writer has ever known was given charge of the burning on a furnace after spending only two days as helper. He spoiled some ware during his first few hours of burning, but in a few days he could be trusted to burn any ware as safely as old burners who had years of experience. Several cases similar to this have been observed, all pointing to the fact that if a man has ordinary intelligence he

can learn to burn enameled ware satisfactorily with very little experience.

The ware is set on pointed projections from iron grates, which should be kept sharp so that the least possible part of the grates comes in contact with the enamel. Only pieces of approximately the same size and weight should be burned together, since only a few minutes are allowed for burning a fork of light steel ware, and if there is much difference in the size of the ware it will heat up to the temperature of the furnace at different rates. As a result of this the lighter ware will be sufficiently fired before larger pieces have acquired the desired temperature, and some of the ware will be sure to be imperfectly fired.

In setting the ware on the grates preparatory to firing, care should be taken to see that ample space is left between all surfaces. Heavy parts like handles on dishpans and ears on kettles should be removed as far as possible from all other surfaces. The reason for this is not only to permit these heavy parts to heat up as rapidly as possible but also to prevent them from absorbing radiated heat from parts near them, thereby retarding the rate at which these parts are heated.

It frequently happens that there will be a small area on a piece of ware underburned while the piece as a whole is properly burned. Investigation of the cause of this will reveal the fact that this underburned spot was in close proximity to some heavy piece of metal or other surface which absorbed the heat while the main body of the piece of ware was free to heat up rapidly. A good burner will strike the happy medium and leave his ware in the furnace long enough to fire the heavy parts properly but not long enough to burn off the light parts. The nature of the enamel influences very materially the burner's ability to properly burn light and heavy parts, but he can greatly facilitate matters by using proper care in setting his ware on the grates.

The temperatures used for burning enamels differ widely, depending upon the enamel and the ware. General practice is to burn the ground coat at much higher temperature than the finishing coats. This is not due to the fact that the ground coat necessarily has a higher softening temperature than the finishing coats, but rather to the fact that it has been found that the general excellence of the ware is improved by this procedure.

(b) Temperature of Burning.—In order to determine the effect of burning at different temperatures, the following series of experiments was performed:

Trial pieces were made of No. 20-gage, United States Standard, open-hearth steel, cut into strips. These were carefully pickled with hydrochloric acid and coated with an enamel which was at that time in commercial use in a factory. The ground coat was applied on both sides of the test pieces by slushing, and two white coats were applied in the same manner on one side. To insure uniformity in application of the enamel, one man dipped all the trials. The ground and white coats used were of the following compositions:

| GROUND-COAT FRIT | |
|---|---|
| Borax | 90 |
| Soda ash | 23 |
| Potash feldspar | 110 |
| Quartz | 70 |
| Manganese dioxide | 18 |
| Saltpeter | 18 |
| Cobalt oxide | 1.5 |
| Fluorspar | 27 |

| MILL ADDITION | | |
|---|---|---|
| Clay | per cent | 8 |
| Water | do | 50 |
| Magnesia | do | .25 |
| Borax in boiling solution | do | 2.0 |

| WHITE-COAT FRIT | |
|---|---|
| Borax | 100 |
| Soda ash | 54 |
| Potash feldspar | 110 |
| Flint | 110 |
| Saltpeter | 23 |
| Fluorspar | 13 |
| Barium carbonate | 25 |
| Antimony oxide | 20 |
| Zinc oxide | 25 |
| Cryolite | 25 |

| MILL ADDITION | | |
|---|---|---|
| Tin oxide | per cent | 6 |
| Clay | do | 6 |
| Magnesium sulphate | do | .5 |

Three different burning temperatures were used for each of the three enamel coats, the furnace temperatures being measured by means of a platinum platinum-rhodium thermocouple. The burning of the trial pieces was intrusted to the best burner in the plant with instructions to obtain the best results on each coat at the given temperatures. The trial pieces were numbered in accordance with the burning temperatures of the three coats. The first digit of the number indicates the temperature used for the ground coat; the second and third digits show the temperatures for the first and second white coats, respectively. The key to the burning temperatures used, with their index numbers and the time required in each case to produce the best results in the enamel, are as follows:

| Ground coat | | | First white | | | Second white | | |
|---|---|---|---|---|---|---|---|---|
| Index No. | Temperature | Time | Index No. | Temperature | Time | Index No. | Temperature | Time |
| | °F | Minutes | | °F | Minutes | | °F | Minutes |
| 1 | 1700 | 4 | 1 | 1600 | 2 | 1 | 1500 | 3 |
| 2 | 1800 | 3 | 2 | 1700 | 1½ | 2 | 1600 | 2 |
| 3 | 1900 | 2 | 3 | 1800 | 1 | 3 | 1700 | 1½ |

The numbering system for the trial pieces shows exactly the burning treatment in each case, as given above and below. The number "111" therefore indicates, by the initial index No. 1, that the ground coat was burned at 1700° F (see table above), and by the second index No. 1, that the first white coat was burned at 1600° F, and the third "1" shows that the second white coat was burned at 1500° F. Likewise trial No. 223 shows automatically that the burning was as follows: "2," ground coat, 1800° F; "2," first white, 1700° F; "3," second white, 1700° F.

BURNING TREATMENTS OF TRIAL PIECES

(For key to numbering system see above)

| | | |
|---|---|---|
| 111 | 211 | 311 |
| 112 | 212 | 312 |
| 113 | 213 | 313 |
| 121 | 221 | 321 |
| 122 | 222 | 322 |
| 123 | 223 | 323 |
| 131 | 231 | 331 |
| 132 | 232 | 332 |
| 133 | 233 | 333 |

The burned trials were examined for surface defects and compared as to gloss and general excellence of quality. Tests were made to determine their ability to withstand abrasion and bending and sudden change of temperature. In the last test several trials were made before comparative results could be obtained. The pieces were heated first to a dull red and plunged into cold water. The trial pieces withstanding this treatment were Nos. 313, 321, 322, 323, 331, 332, 333, 231, and 131. Nos. 311 and 312 were only slightly chipped.

In the bending test the trial pieces were bent around a 1¼-inch pipe with the white-coated surface on the inside. The following trials withstood this test without indication, to the unaided eye, of rupture: Nos. 111, 121, 231, 331, and 332, showing excellent toughness and flexibility of the enamel. All the trials withstood bending to a right angle before the enamel came off.

In examining the pieces for surface defects, gloss, and general excellence of quality, it was noted that the best appearance was always obtained with the lowest temperature of burning of the final coat, regardless of the treatment for the preceding coats. Black specks and dull enamels resulted from high temperatures of burning the finish coat.

The following conclusions were drawn from the results of the tests:

1. The test pieces on which the ground coat was burned at the highest temperature were best able to withstand sudden change of temperature.

2. The ability of the enamel to withstand abrasion, bending, or sudden change of temperature is greatest when the temperature at which the finishing coat is burned is decidedly lower than that at which one of the preceding coats has been burned.

3. A low temperature can be used for burning the ground coat, provided it is burned "done," and a high temperature is used for burning first coat white.

4. To prevent pinholes and black specks a high heat should be used for either ground coat or first coat white, and a much lower heat for finish white.

For best results with this enamel, the ground coat should not be burned below 1700° F, and the first coat white should be nearly as high. The finish white should be burned at a temperature at least 100° below either the ground coat or the first coat white. Temperatures recommended for these enamels are about as follows: Ground coat, 1800° F; first white coat, 1750 to 1800° F; finish white, 1600 to 1650° F.

While the results obtained here can be strictly applied to these enamels only, experience in using many other enamels confirms the conclusions reached in this series of experiments.

Obviously no fixed rule can be laid down for burning enamel wares, since different shapes and sizes can be best burned under different conditions. The production of some enamels requires high temperatures for burning, and, unfortunately, these enamels are sometimes applied to very large pieces, which have a great tendency to warp during burning. Furthermore, it is commonly the case that several pieces must be joined after enameling, this fact making it essential that the warpage be reduced to a minimum. Since the tendency to warp increases with increase of temperature, it will be readily seen that the production of this class of ware requires the striking of a medium as regards time and temperature of burning which will give an enamel of the desired quality while at the same time causing little warpage of the ware.

In making cooking utensils and some other shapes of light-gage steel, the wire is straightened while still hot after coming from the furnace. Warpage will be greatly reduced by using proper

care in supporting the ware during burning. Every precaution should be taken to see that the ware is supported at a sufficient number of points and at proper points to prevent warping.

Just as emphasis was laid on the proper slushing of first coats of enamels, so also must the importance of proper burning of the first coat be emphasized. Improper burning of the first coat produces a large amount of defective ware. It is essential that the first coat be properly and uniformly applied in order to be properly burned, but proper burning is absolutely necessary if a good piece of ware is to result. This is left to the judgment of the burner, who estimates from the appearance of the specimen when it has been properly burned. Proper burning can be accomplished at different temperatures by suitable adjustment of the time.

The first coat, when properly burned, seldom has a high luster, but will not be dead. A blue or purple color indicates underburning, which will result in "fish scale" or jumping off upon application of the cover coat. A dead-black or a green color indicates overburning, which will be difficult to cover with white and may result in jumping off or in fish scale of a type different from that of underburning. Fish scale on underburned ware generally results in flakes from one-sixteenth to one-eighth inch in diameter jumping off, while fish scale from overburning results in very minute flakes popping off in great numbers. Running the hand over a piece of overburned ware produces a snapping sound. Sometimes the fish scaling will not start until the first coat of white is run into the furnace, or fish scaling may not develop at all, but the enamel will not adhere properly and the ware is sure to be short-lived.

## VI. CALCULATION OF ENAMEL FORMULAS

### 1. METHODS EMPLOYED

Several methods of expressing quantitatively the compositions of glasses, glazes, and enamels have been devised. In most of these it is the purpose to indicate the relative proportions of the components remaining after the melting process, in which volatile matter is expelled from the raw ingredients. Among the methods of expressing compositions are:

1. Composition in Percentages of Raw Materials Used.—This corresponds to the batch weights and does not attempt to show the composition of the finished product. An advantage is claimed for this method in that it recognizes differences in effect

of various raw materials which may be so combined as to produce the same final product, so far as chemical analysis would show in various mixtures, but in which these different materials produce different melting behaviors and possibly different physical properties.

2. Composition in Percentages of the Oxides in the Product.—This corresponds to the result obtained by chemical analysis.

3. Composition in Terms of Eutectics.—Some use of combinations of eutectic mixtures of various oxides or minerals has been made to produce fusible compositions for glazes.[17] Owing to the lack of information on the eutectics formed between components used in enamel mixtures, this method is not at present practical for expressing enamel formulas.

4. Composition in Terms of Norms.[18]—This attempts to express the formula in terms of minerals considered as most likely to be formed in the fusion of the raw materials used in the mixture. It has been proposed for use in compounding glazes but has not been applied to enamels.

5. Empirical Formula.—This attempts to represent the composition of the fusion product of a mixture in molecular proportions of the oxides present. Regarding this method, objection is made that it attempts but does not realize the representations of the chemical constitution, and that it is unscientific and cumbersome. It may be noted in this connection that many of our chemical formulas do not express actual compositions but only relative proportions of elements. Their value is not, however, lost by this fact. The empirical glaze, or enamel formula, is merely a means of expression and a tool which has proved valuable as an aid to study and comparison of various combinations of materials.

## 2. COMPOSITION IN TERMS OF OXIDES

The fritted weight of an enamel may be closely approximated by calculating the quantity of oxide capable of being formed by the elements incorporated into the batch. Several factors enter into fritting which make it impossible to figure the exact weight of frit obtainable from a given quantity of raw material of which the exact composition is known. Among these may be mentioned

[17] Watts, A. S., A Study of Bristol Glazes Compounded on the Eutectic Basis, Trans. Am. Ceram. Soc., 18, 1916. The Practical Application of Bristol Glazes Compounded on the Eutectic Basis, Trans. Am. Ceram. Soc., 19, 1917.

[18] Stull, H. F., The Calculation of Ceramic Mixtures, Trans. Am. Ceram. Soc., 13, 1911.

loss during charging the smelter by chemicals being carried away by the draft, volatilization of some of the metallic elements, and lack of complete decomposition of some of the raw materials, notably fluorides. However, in spite of these discrepancies, the calculated fritted weight will generally approximate quite closely the actual weight obtained.

In enamel calculations it is assumed that the following materials are not volatile: silica, flint, sand, $SiO_2$; zinc oxide, ZnO; litharge, PbO; tin oxide, $SnO_2$. Antimony is more or less volatile, according to the conditions and intensity of heat treatment during melting. In calculating formulas the usual practice is to assume that 100 per cent is retained.

The accompanying table (Table 2), based upon chemically pure materials, shows the fritted weight of the oxides obtained when the other raw materials ordinarily used in enamels are completely decomposed under the influence of heat in an oxidizing atmosphere.

**TABLE 2.—Fritted Weights as Per Cent of Weight of Pure Raw Material**

| Material | Potassium oxide ($K_2O$) | Sodium oxide ($Na_2O$) | Calcium oxide (CaO) | Magnesium oxide (MgO) | Lead oxide (PbO) | Barium oxide (BaO) | Aluminum oxide ($Al_2O_3$) | Silicon dioxide ($SiO_2$) | Boric oxide ($B_2O_3$) |
|---|---|---|---|---|---|---|---|---|---|
| Feldspar | 17 | | | | | | 18 | 65 | |
| Red lead | | | | | 97 | | | | |
| White lead | | | | | 86 | | | | |
| Barium carbonate | | | | | | 78 | | | |
| Calcium carbonate | | | 56 | | | | | | |
| Fluorspar [a] | | | 72 | | | | | | |
| Cryolite [a] | | 44 | | | | | 24 | | |
| Soda ash | | 58 | | | | | | | |
| Sodium nitrate | | 36 | | | | | | | |
| Saltpeter or potassium nitrate | 47 | | | | | | | | |
| Magnesium carbonate | | | | 48 | | | | | |
| Borax | | 16.2 | | | | | | | 36.6 |
| Boracic acid | | | | | | | | | 56.4 |
| Clay | | | | | | | 39 | 47 | |

[a] The fritted product obtained from fluorides is variable and uncertain. The values given are based on the assumption that the fluorides are completely decomposed.

The following illustrates the use of the table in finding the fritted weight of an enamel:

| | Pounds raw | Per cent of oxides | Pounds frit | Pounds lost |
|---|---|---|---|---|
| | | 17.0 | 17.0 $K_2O$ | |
| Feldspar | 100 | 18.0 | 18.0 $Al_2O_3$ | |
| | | 65.0 | 65.0 $SiO_2$ | |
| Flint | 100 | 100.0 | 100.0 $SiO_2$ | |
| | | 16.2 | 16.2 $Na_2O$ | |
| Borax | 100 | 36.6 | 36.6 $B_2O_3$ | |
| | | 47.2 | | 47.2 $H_2O$ |
| Soda ash | 50 | 58.0 | 29.0 $Na_2O$ | |
| | | 42.0 | | 21.0 $CO_2$ |
| | | 47.0 | 4.7 $K_2O$ | |
| Saltpeter | 10 | 45.0 | | 4.5 $NO_2$ |
| | | 8.0 | | .8 $O_2$ |
| Fluorspar | 30 | 72.0 | 21.6 CaO | |
| | | 19.0 | | 14.7 F |
| | | 44.0 | 22.0 $Na_2O$ | |
| Cryolite | 50 | 24.0 | 12.0 $Al_2O_3$ | |
| | | 54.0 | | 22.0 F |
| Antimony oxide | 40 | 100.0 | 40.0 $Sb_2O_3$ | |
| Tin oxide | 20 | 100.0 | 20.0 $SnO_2$ | |
| Zinc oxide | 15 | 100.0 | 15.0 ZnO | |
| Total | 525 | | 417.1 | 110.2 |

The calculation of the fritted weight of an enamel can be simplified by use of the curves in Fig. 7. Each curve shows the weight of one oxide per 100 pounds of the raw material introduced, or the percentage of the original weight.

Illustration: To find the fritted weight of a white enamel of the following composition:

| | | | |
|---|---|---|---|
| Feldspar | 178.0 | Fluorspar | 10.5 |
| Flint | 140.0 | Cryolite | 59.5 |
| Borax | 83.0 | Tin oxide | 34.0 |
| Soda ash | 15.0 | | |
| Saltpeter | 16.0 | | 536.0 |

Feldspar is found represented on three curves, 2, *x*, and 15, showing the weight of potassium oxide, alumina, and silica, respectively, resulting from the fritting of 100 pounds of feldspar.

To determine the weight of potassium oxide resulting from the 178 pounds of feldspar used, follow the horizontal line corresponding to 178 pounds raw material to the right until it intersects curve No. 2; then drop vertically and read the pounds of oxide on the base line, in this case 30. Following the same procedure it is found that the horizontal line corresponding to 178 pounds of raw

material intersects curves *x* and 15 on vertical lines corresponding to 32 and 115.5 pounds of alumina and silica, respectively. The same method is followed for the other raw materials. In some cases the intersection of the curves falls near the lower left-hand corner of the sheet, where the exact location of the point is difficult

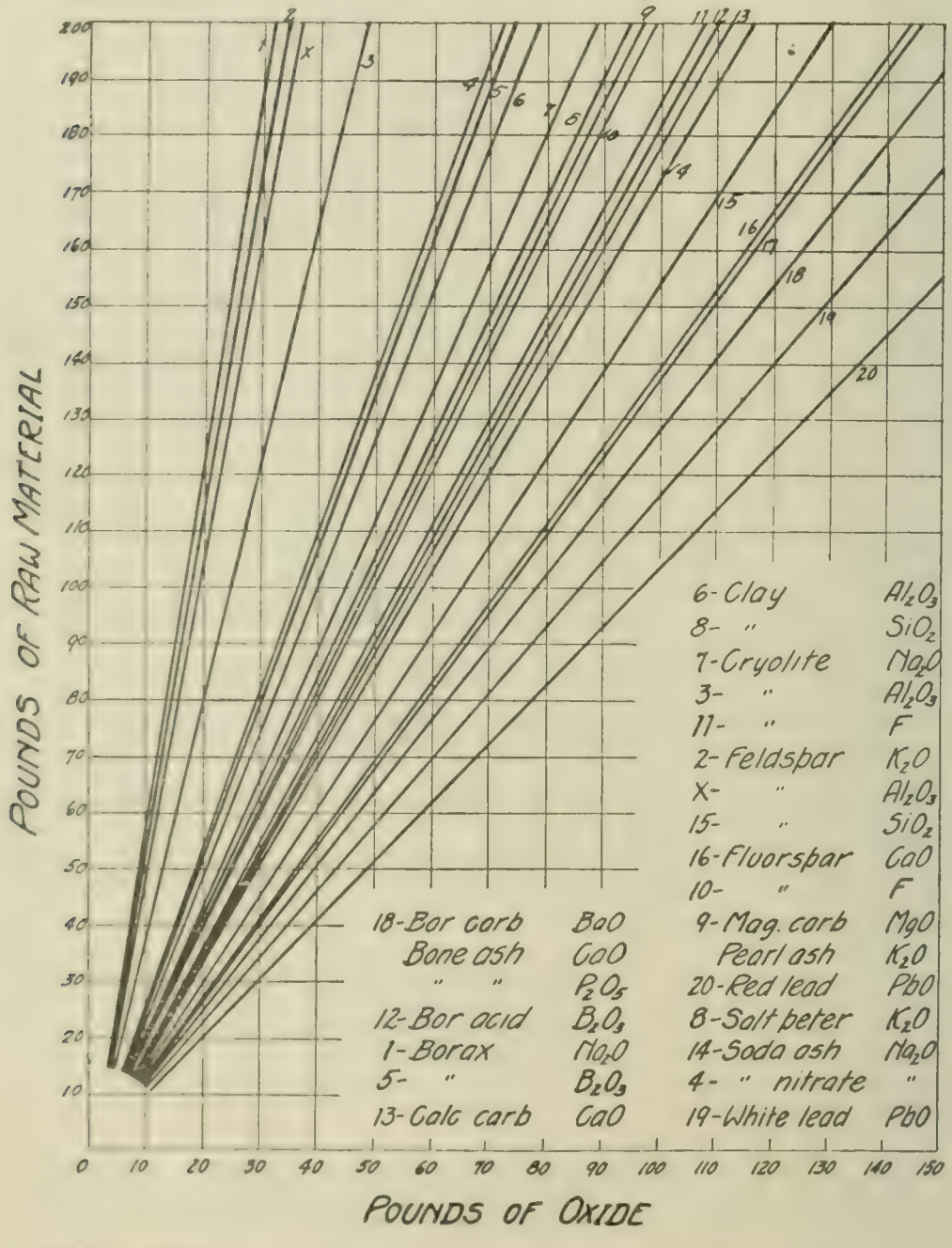
POUNDS OF RAW MATERIAL
POUNDS OF OXIDE
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
6-Clay $Al_2O_3$
8- " $SiO_2$
7-Cryolite $Na_2O$
3- " $Al_2O_3$
11- " F
2-Feldspar $K_2O$
X- " $Al_2O_3$
15- " $SiO_2$
16-Fluorspar CaO
10- " F
9-Mag. carb MgO
Pearl ash $K_2O$
20-Red lead PbO
8-Salt peter $K_2O$
14-Soda ash $Na_2O$
4- " nitrate "
19-White lead PbO
18-Bor carb BaO
Bone ash CaO
" " $P_2O_5$
12-Bor acid $B_2O_3$
1-Borax $Na_2O$
5- " $B_2O_3$
13-Calc carb CaO

FIG. 7.—*Chart for obtaining pounds of oxide from pounds of raw material*

to determine. In such a case a multiplier may be used for the raw material and the same number will then be used as a divisor for the resulting weight of the oxide. Thus, in the case of soda ash, the intersection of the horizontal line for 15 pounds of raw material with curve 14 is not easily determined, but the weight of soda ash may be multiplied by 10. The weight of sodium oxide resulting

from 150 pounds of the ash is 87 pounds. Then, dividing this by 10, the amount of sodium oxide derived from 15 pounds of the ash is 8.7 pounds. Other multipliers may be used when convenient.

Following the same procedure for all the raw materials in the batch, the results obtained may be tabulated as follows. The fritted weight is obtained by adding the weights of the oxides. The composition may be expressed in percentage of the oxides by dividing the weight of each by the fritted weight of the enamel:

| Batch | Potassium oxide ($K_2O$) | Sodium oxide ($Na_2O$) | Calcium oxide (CaO) | Alumina ($Al_2O_3$) | Boric oxide ($B_2O_3$) | Silica ($SiO_2$) | Tin oxide ($SnO_2$) | Fluorine (F) |
|---|---|---|---|---|---|---|---|---|
| 178 feldspar | 30.0 | | | 32.0 | | 115.5 | | |
| 140 flint | | | | | | 140.0 | | |
| 83 borax | | 13.0 | | | 31.0 | | | |
| 15 soda ash | | 8.7 | | | | | | |
| 16 saltpeter | 7.5 | | | | | | | |
| 10.5 fluorspar | | | 7.5 | | | | | 5.2 |
| 59.5 cryolite | | 26.0 | | 14.0 | | | | 32.0 |
| 34 tin oxide | | | | | | | 34.0 | |
| Fritted weight | 37.5 | 47.7 | 7.5 | 46.0 | 31.0 | 255.5 | 34.0 | 37.2 |
| Percentage composition | 7.56 | 9.60 | 1.51 | 9.27 | 6.25 | 51.46 | 6.85 | 7.50 |

These curves are based on chemically pure materials, but similar curves may be drawn for any substance of known composition. Allowance may also be made for the moisture content of a material in the preparation of such curves.

### 3. MOISTURE FACTOR

It is frequently the case that raw materials for enamels contain considerable percentages of moisture. In order to maintain correct compositions it is necessary to make allowance for the moisture content in making up the batch. The moisture content is easily determined by weighing a sample of a material, carefully drying it, then weighing the dried material. The percentage loss is generally based on the weight of dry material. The moisture factor represents the weight of raw material necessary to give 1 pound of dry material or $\left(1+\frac{x}{100}\right)$ where $x$ = per cent moisture content in terms of dry weight.

For example, a sample of flint from the bin weighs 10 pounds before and 9 pounds after drying, the moisture loss being 1 pound. The moisture content in percentage of dry weight is $\frac{1}{9}\times 100 = 11.1$ per cent. In order to obtain a definite weight of dry flint, the

weight of material taken from the bin must be $\frac{10}{9} = 1 + \frac{11.1}{100} = 1.11$ times the dry weight required. This figure 1.11 represents the moisture factor in this case. If the moisture were not taken into account in preparing an enamel batch with such flint, there would be a very appreciable error in the composition of the enamel. Such a moisture factor in powdered flint or quartz is uncommon, but the importance of determining the moisture content of raw materials is obvious

#### 4. EMPIRICAL FORMULA

The empirical formula, or the ceramic formula, as it is sometimes called, has been found to be a convenient means of representing the compositions of ceramic materials, minerals, etc., as well as those of glazes and enamels. The computation of the empirical formula is not a difficult matter and requires only a limited knowledge of chemistry, principally the symbols and atomic weights of the elements.

All chemical compounds are made up of elementary substances or elements, which are distinct kinds of matter. The compounds are formed by combination of the elements in definite proportions. As a matter of convenience the kinds and amounts of the elements forming a compound are represented by symbols and numerical factors. Each element is represented by a letter symbol, as Al for aluminum and O for oxygen. These symbols indicate that certain definite relative weights of the elements for which they stand are present in the compound. Thus the symbol Al represents 27 parts by weight of aluminum. This weight is known as the atomic weight. When more than one atomic weight of an element is present in a compound, this is indicated by numerical subscripts. Thus, alumina, which is made up of 2 atoms, by weight, of aluminum and 3 of oxygen, is written $Al_2O_3$, the subscripts following the symbol of each element showing the number of atoms of that substance in the compound. Silica is represented by $SiO_2$, water by $H_2O$, etc.

From the relative weights of the elements—atomic weights—and the number of atoms of each in the compound, the relative weight of the compound—molecular weight—may be calculated. Thus the molecular weight of $Al_2O_3$ is $(2 \times 27) + (3 \times 16) = 102$; of $SiO_2$ $28 + (2 \times 16) = 60$, etc. The term "formula weight" may be used instead of molecular weight for ceramic calculations. The formula weight of a compound or molecule is simply the weight indicated by the formula. Often several compounds or

molecules are united to form a more complex compound or molecule.

The accompanying table gives the names, symbols, and atomic weights in round numbers of the elements commonly found in enamels. For a more complete list textbooks on chemistry should be consulted.

**TABLE 3.—Atomic Weights of Elements Commonly Found in Enamels**

| Element | Symbol | Atomic weight | Element | Symbol | Atomic weight |
|---|---|---|---|---|---|
| Aluminum | Al | 27 | Magnesium | Mg | 24 |
| Antimony | Sb | 120 | Manganese | Mn | 55 |
| Barium | Ba | 137 | Nickel | Ni | 59 |
| Boron | B | 11 | Nitrogen | N | 14 |
| Calcium | Ca | 40 | Oxygen | O | 16 |
| Carbon | C | 12 | Phosphorus | P | 31 |
| Chromium | Cr | 52 | Potassium | K | 39 |
| Cobalt | Co | 59 | Silicon | Si | 28 |
| Copper | Cu | 64 | Sodium | Na | 23 |
| Fluorine | F | 19 | Sulphur | S | 32 |
| Hydrogen | H | 1 | Tin | Sn | 119 |
| Iron | Fe | 56 | Zinc | Zn | 65 |
| Lead | Pb | 207 | | | |

The empirical formula expresses the composition in molecular proportions of the various oxides which would be obtained by chemical analysis rather than in terms of the ratio of atoms of the elements present. Thus, the chemical formula of orthoclase or microcline may be written as

$KAlSi_3O_8$—chemical formula,

or

$K_2O.Al_2O_3.6\ SiO_2$—ceramic formula.

The latter is much more conveniently used in ceramic calculations. It represents the composition as being in the ratio of 1 molecule of potassium oxide to 1 of alumina to 6 of silica. Similarly the formula of borax may be written in the two ways as

$$Na_2B_4O_7.10H_2O$$

or

$$Na_2O.2B_2O_3.10H_2O.$$

The empirical, or ceramic, formula of a material is calculated from the chemical analysis in the following manner: The percentage, by weight, of each oxide is divided by its molecular weight, giving the relative molecular proportion of each in the material. In order to obtain a definite basis for comparison and use of such compositions, some portion of the formula is expressed

as unity, generally the sum of the basic oxides. Using the sum of the molecular proportions of the basic oxides as a divisor, the value obtained for each oxide is divided by this amount to obtain the ratio of molecular parts in terms of basic oxides as 1. An example of the method is as follows:

CHEMICAL ANALYSIS OF FELDSPAR

Potassium oxide, $K_2O$ = 16.9 per cent by weight;
Aluminum oxide, $Al_2O_3$ = 18.4 per cent by weight;
Silicon dioxide, $SiO_2$ = 64.7 per cent by weight.

Dividing the percentage of each oxide by its molecular weight gives

$K_2O$ . . . . . 16.9 ÷ 94 = 0.18 molecular parts;
$Al_2O_3$ . . . . . 18.4 ÷ 102 = .18 molecular parts;
$SiO_2$ . . . . . 64.7 ÷ 60 = 1.08 molecular parts.

To express the molecular ratio of oxides in terms of basic oxides as unity, divide the above values by that of $K_2O$:

$$\frac{0.18}{0.18} = 1\ K_2O \quad \frac{0.18}{0.18} = 1\ Al_2O_3 \text{ and } \frac{1.08}{18} = 6\ SiO_2.$$

The empirical formula is $K_2O\ Al_2O_3\ 6SiO_2$.

The empirical formula of any material, including that of an enamel, may be calculated from its percentage composition in the same manner.

## 5. CALCULATION OF EMPIRICAL FORMULA FROM CHEMICAL ANALYSIS

The analysis of an enamel is as follows:

| | | | |
|---|---|---|---|
| $K_2O$ | 6.5 | $Al_2O_3$ | 4.7 |
| $Na_2O$ | 17.5 | $SiO_2$ | 43.3 |
| BaO | 5.5 | $B_2O_3$ | 10.0 |
| ZnO | 6.0 | $SnO_2$ | 7.5 |
| CaO | 5.6 | | |

The relative molecular proportions of the oxides is determined by dividing the percentage of each by its molecular weight:

6.5 ÷ 94. = 0.069 $K_2O$;
17.5 ÷ 62. = 0.280 $Na_2O$;
5.5 ÷ 153. = 0.036 BaO;
6.0 ÷ 81. = 0.074 ZnO;
5.6 ÷ 56. = 0.100 CaO;
4.7 ÷ 102. = 0.046 $Al_2O_3$;
43.3 ÷ 60. = 0.721 $SiO_2$;
10. ÷ 70. = 0.143 $B_2O_3$;
7.5 ÷ 151. = 0.050 $SnO_2$.

MOLECULAR RATIO OF OXIDES

$$\left.\begin{matrix}0.069\ K_2O\\ .280\ Na_2O\\ .036\ BaO\\ .074\ ZnO\\ .100\ CaO\end{matrix}\right\}0.046\ Al_2O_3\left\{\begin{matrix}0.721\ SiO_2\\ .143\ B_2O_3\\ .050\ SnO_2\end{matrix}\right.$$

.559—sum of basic oxides.

Dividing through by 0.559 to obtain the ratio on the basis of unit basic oxides (RO), the empirical formula is obtained:

$$\left.\begin{matrix}0.123\ K_2O\\ .502\ Na_2O\\ .064\ BaO\\ .132\ ZnO\\ .179\ CaO\end{matrix}\right\}0.082\ Al_2O_3\left\{\begin{matrix}1.28\ SiO_2\\ .25\ B_2O_3\\ .09\ SnO_2\end{matrix}\right.$$

1.000

The accompanying table (Table 4) gives the name, ceramic formula, molecular weight, and melted weight of pure raw materials ordinarily used in enamels.

**TABLE 4.—Description of Pure Enameling Raw Materials**

| Name | Ceramic formula | Formula weight | Fusion product | Melted weight |
|---|---|---|---|---|
| Alumina | $Al_2O_3$ | 102 | $Al_2O_3$ | 102 |
| Antimony oxide | $Sb_2O_3$[a] | 287 | $Sb_2O_3$[a] | 287 |
| Barium carbonate | $BaCO_3$ | 197 | BaO | 153 |
| Boric acid | $B_2O_3\ 3H_2O$ | 120 | $B_2O_3$ | 70 |
| Boric oxide | $B_2O_3$ | 70 | $B_2O_3$ | 70 |
| Calcium carbonate<br>Carbonate of lime | $CaCO_3$ | 100 | CaO | 56 |
| Calcium fluoride<br>Fluorspar | $CaF_2$ | 78 | CaO | 56 |
| Quicklime | CaO | 56 | CaO | 56 |
| Calcium phosphate<br>Bone ash | $3\ CaO\ P_2O_5$ | 310 | 3CaO | 3×56=168 |
| Chromium oxide | $Cr_2O_3$ | 153 | $Cr_2O_3$ | 153 |
| Cobalt oxide | $Co_3O_4$ | 123 | $Co_3O_4$ | 123 |
| Copper oxide | CuO | 80 | CuO | 80 |
| Iron oxide (red) | $Fe_2O_3$ | 160 | $Fe_2O_3$ | 160 |
| White lead<br>Basic lead carbonate | $Pb(OH)_2 2PbCO_3$ | 775 | 3PbO | 3×223=669 |
| Lead oxide (yellow)<br>Litharge | PbO | 223 | PbO | 223 |
| Lead oxide (red)<br>Minium | $Pb_3O_4$ | 685 | 3PbO | 3×223=669 |
| Carbonate of magnesia | $MgCO_3$ | 84 | MgO | 40 |
| Magnesia | MgO | 40 | MgO | 40 |
| Manganese dioxide | $MnO_2$ | 87 | $MnO_2$ | 87 |
| Black oxide of nickel | $Ni_2O_3$ | 165 | $Ni_2O_3$ | 165 |

[a] It is customary to consider commercial oxides as being $Sb_2O_3$. In reality they are mainly $Sb_2O_4$, formula weight 303. Probably during fusion antimony oxide is converted to the pentoxide, $Sb_2O_5$, in which case the melted weight is 321.

TABLE 4—Continued

| Name | Ceramic formula | Formula weight | Fusion product | Melted weight |
|---|---|---|---|---|
| Potassium carbonate | $K_2CO_3$ | 138 | $K_2O$ | 94 |
| Pearl Ash | | | | |
| Potassium nitrate (saltpeter) | $KNO_3$ | 101 | $K_2O$ | 94 |
| | $K_2O\ N_2O_5$ | 202 | $K_2O$ | 94 |
| Sodium borate | $Na_2O\ 2B_2O_3\ 10H_2O$ | 382 | $Na_2O\ 2B_2O_3$ | 202 |
| Borax | | | | |
| Soda ash | $Na_2CO_3$ | 106 | $Na_2O$ | 62 |
| Sodium carbonate crystals | $Na_2CO_3\ 10H_2O$ | 286 | $Na_2O$ | 62 |
| Sodium nitrate (Chili saltpeter) | $NaNO_3$ | 85 | $Na_2O$ | 62 |
| | $Na_2O\ N_2O_5$ | 170 | | 62 |
| Silica: | | | | |
| Flint | $SiO_2$ | 60 | $SiO_2$ | 60 |
| Quartz | | | | |
| Sand | | | | |
| Silicon fluoride | $SiF_4$ | 104 | $SiO_2$ | 60 |
| Tin oxide (white) | $SnO_2$ | 151 | $SnO_2$ | 151 |
| Zinc oxide | $ZnO$ | 81 | $ZnO$ | 81 |
| Feldspar (orthoclase) | $K_2O\ Al_2O_3\ 6SiO_3$ | 556 | $K_2O\ Al_2O_3\ 6SiO_2$ | 556 |
| Clay (kaolinite) | $Al_2O_3\ 2SiO_2\ 2H_2O$ | 258 | $Al_2O_3\ 2SiO_2$ | 222 |
| Cryolite | $6NaF\ Al_2F_6$ | 420 | $3Na_2O\ Al_2O_3$ | 282 |

## 6. CALCULATION OF EMPIRICAL FORMULA FROM BATCH WEIGHTS

The calculation of the empirical formula of an enamel from the batch weights of the raw materials is made similarly to the calculation from analysis. In the following calculations the weight of each raw material used in the batch is divided by its formula weight to obtain the molecular proportions used. This value, multiplied by the number of molecular parts of each oxide in the formula, gives the number of molecular parts of each introduced into the enamel by the given material. Summing the values obtained for each oxide from the various raw materials, and dividing through by the total molecular parts of the basic oxides (to obtain unit basic oxides or 1 RO), the empirical formula is obtained.

| Material | Formula | Formula weight | Batch weight | Molecular parts |
|---|---|---|---|---|
| Feldspar | $K_2O.Al_2O_3.6SiO_2$ | 556 | 100 | $100 \div 556 = 0.18$ |
| Flint | $SiO_2$ | 60 | 100 | $100 \div 60 = 1.67$ |
| Borax | $Na_2O.2B_2O_3.10H_2O$ | 382 | 110 | $110 \div 382 = .288$ |
| Soda ash | $Na_2CO_3$ | 106 | 50 | $50 \div 106 = .472$ |
| Saltpeter | $(KNO_3)_2$ | 202 | 25 | $25 \div 202 = .123$ |
| Fluorspar | $CaF_2$ | 78 | 45 | $45 \div 78 = .577$ |
| Cryolite | $6NaF.Al_2F_6$ | 420 | 20 | $20 \div 420 = .048$ |
| Zinc oxide | $ZnO$ | 81 | 5 | $5 \div 81 = .062$ |
| Antimony oxide | $Sb_2O_3$ | 287 | 20 | $20 \div 287 = .070$ |

The molecular proportions of oxides resulting is as follows:

| Molecular parts | Raw material | Formula | $K_2O$ | $Na_2O$ | CaO | ZnO | $Al_2O_3$ | $B_2O_3$ | $Sb_2O_3$ | $SiO_2$ | F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.180 | Feldspar | $K_2O.Al_2O_3.6SiO_2$ | 0.18 | | | | 0.18 | | | 1.08 | |
| 1.670 | Flint | $SiO_2$ | | | | | | | | 1.67 | |
| .288 | Borax | $Na_2O.2B_2O_3 10H_2O$ | | 0.288 | | | | 0.576 | | | |
| .472 | Soda ash | $Na_2CO_3$ | | .472 | | | | | | | |
| .123 | Saltpeter | $(KNO_3)_2$ | .123 | | | | | | | | |
| .577 | Fluorspar | $CaF_2$ | | | 0.577 | | | | | | 1.154 |
| .048 | Cryolite | $6NaF.Al_2F_6 = 3Na_2O.Al_2O_3.12F$. | | .144 | | | .048 | | | | .576 |
| .062 | Zinc oxide | ZnO | | | | 0.062 | | | | | |
| .070 | Antimony oxide | $Sb_2O_3$ | | | | | | | 0.070 | | |
| Molecular parts of basic oxides | | | .303 | .904 | .577 | .062 | .228 | .576 | .070 | 2.75 | 1.730 |

The sum of the molecular parts of basic oxides = 1.846 = value to be used as divisor.

The empirical formula of this enamel is

$$\left.\begin{matrix} 0.163\ K_2O \\ .490\ Na_2O \\ .313\ CaO \\ .034\ ZnO \end{matrix}\right\} 0.124\ Al_2O_3 \left\{\begin{matrix} 1.490\ SiO_2 \\ .312\ B_2O_3 \\ .937\ F \\ .038\ Sb_2O_3 \end{matrix}\right.$$

1.000

## 7. CALCULATION OF BATCH WEIGHTS FROM THE EMPIRICAL FORMULA

In outlining a series of experiments for the purpose of studying enamels with reference to the effect of some one ingredient or a number of ingredients, the empirical formula has been found useful by certain investigators. It is of importance, therefore, to know how to figure batch compositions from empirical formulas. The process is just the reverse of that of figuring formulas from batch weights. The only point likely to lead to confusion is the fact that the same oxide can be derived from several different raw materials, and care must be exercised in selecting the raw materials to use. The following examples illustrate the procedure:

Given the formula of an enamel, to calculate the batch weights. Formula:

$$\left.\begin{matrix} 0.09\ K_2O \\ .62\ Na_2O \\ .10\ CaO \\ .10\ BaO \\ .09\ ZnO \end{matrix}\right\} 0.20\ Al_2O_3 \left\{\begin{matrix} 1.60\ SiO_2 \\ .50\ B_2O_3 \\ 1.52\ F \\ .10\ Sb_2O_3 \end{matrix}\right.$$

1.00

Evidently the $K_2O$ can be obtained from feldspar or $KNO_3$; the $Na_2O$ can be obtained from soda ash, borax, cryolite, sodium nitrate, soda feldspar, etc.; the CaO from $CaCO_3$, $CaF_2$, $CaSO_4$, etc.; $Al_2O_3$ from feldspar, clay, or cryolite; $B_2O_3$ from borax or boric acid. From this it will be seen that there is considerable freedom in choice of raw materials to obtain the final result. It is therefore necessary to first decide what raw materials are to be used in making the enamel. The following assumptions are made: All $B_2O_3$ is to be derived from borax; all $K_2O$ from feldspar, assumed to be pure orthoclase; all F from fluorspar and cryolite; all CaO from fluorspar; all BaO from barium carbonate; ZnO from zinc oxide; $Sb_2O_3$ from antimony oxide. Flint and clay will be used if necessary to fulfill the requirements for $Al_2O_3$ and $SiO_2$.

For convenience the calculations are arranged in tabular form. The amount of oxide added by each ingredient of the batch is subtracted from the required amount in the column for the oxide, and the difference indicates further requirements to be obtained from other sources. The weight of each raw material used is the product of the molecular parts used times its formula weight and is recorded in the column of batch weights.

| Formula | | | | | | | | | | Material used | Molecular parts | Formula weight | Batch weight |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_2O$ | $Na_2O$ | CaO | BaO | ZnO | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ | F | $Sb_2O_3$ | | | | |
| 0.09 | 0.62 | 0.10 | 0.10 | 0.09 | 0.20 | 1.60 | 0.50 | 1.52 | 0.10 | Feldspar, $K_2O$, $Al_2O_3$, $6SiO_2$ | 0.09 | ×556 | 50.04 |
| .09 | | | | | .09 | .54 | | | | | | | |
| | | | | | .11 | 1.06 | | | | Borax, $Na_2O$, $2B_2O_3$, $10H_2O$ | .25 | ×382 | 95.50 |
| | .25 | | | | | | .50 | | | | | | |
| | .37 | | | | | | 0 | | | Cryolite, 6NaF, $Al_2F_6$ | .11 | ×420 | 46.20 |
| | .33 | | | | .11 | | | 1.32 | | | | | |
| | .64 | | | | 0 | | | .20 | | Fluorspar $CaF_2$ | .10 | × 78 | 7.80 |
| | | .10 | | | | | | .20 | | | | | |
| | | 0 | | | | | | | | Barium Carbonate, $BaCO_3$ | .10 | ×197 | 19.70 |
| | | | .10 | | | | | | | | | | |
| | | | 0 | | | | | | | Zinc oxide, ZnO | .09 | × 81 | 7.29 |
| | | | | .09 | | | | | | | | | |
| | | | | 0 | | | | | | Antimony oxide, $Sb_2O_3$ | .10 | ×287 | 28.70 |
| | | | | | | | | | .10 | | | | |
| | | | | | | | | | | Flint, $SiO_2$ | 1.06 | × 60 | 60.36 |
| | | | | | | 1.06 | | | | | | | |
| | | | | | | 0 | | | | Sodium nitrate, $(NaNO_3)_2$ | .04 | ×170 | 6.80 |
| | .64 | | | | | | | | | | | | |
| | | | | | | | | | | | | | 322.39 |

It is entirely possible to make up the same formula by use of other raw materials than those selected here. The selections will depend upon the materials available, and in some cases it may be found impossible to compound an enamel of given composition from those at hand. In such a case it will, of course, be necessary either to change the formula or to obtain other materials by which the requirements may be fulfilled.

The methods of calculation illustrated refer to the frit only. While the enamel frit is a more or less homogeneous glass, and variations in the formula of the frit represent variations in its physical character, the raw materials added to it seldom become thoroughly combined with it during the burning of the ware. While the formula of the finished enamel is sometimes given, there is seldom any gain in recasting the formula for the purpose of including in it the raw materials added in the mill. When it is desired to reproduce a steel enamel from the formula, it is generally safe to assume that all the tin oxide was added raw and that sufficient of the alumina and silica of the formula came from raw clay to amount to about 8 per cent clay at the mill. All other ingredients of the formula can be assumed as fritted without any appreciable error being introduced. While some of these might have been added raw, the amount will be so small as to be negligible so far as reproduction of the formula is concerned.

Obviously, special cases may arise where this assumption can not be safely made, for instance, in the case of many colored enamels where coloring oxides are added in the mill. In such cases the color obtained will be quite different when the coloring oxide is fritted. In the reproduction of any color, experience and experiments are necessary.

### 8. USE OF CURVES IN CALCULATING FORMULAS FROM BATCH WEIGHTS

A brief survey of the above outline of methods of calculating the empirical formula is sufficient to convince one of the justice of the criticism that it is a laborious process. The accompanying set of curves (Figs. 8, 9, 10, 11) greatly simplify the use of empirical formulas. By the use of these curves the work required to figure the formula is exactly the same as that required to figure the percentage composition. Likewise the work of calculating the batch weights from the formula is exactly the same as that required to figure the batch weights from the percentage composition of the oxides.

These curves are obtained by making the arithmetical calculation necessary to determine one point and then drawing a straight line through the point determined and zero.

Thus, to find the curve for formula weights of $B_2O_3$, from borax ($Na_2O$ 2 $B_2O_3$ 10 $H_2O$), formula (molecular) weight 382:

Assume 100 borax: $100 \div 382 - 0.262$ formula weight of borax. One formula weight of borax gives 2 formula weights of $B_2O_3$.

$0.262 \times 2 = 0.524$ formula weight $B_2O_3$ from 100 borax.

To draw the curve: On the horizontal line representing 100 raw material, run across to the vertical line corresponding with 0.524 formula weight of oxide. Draw a straight line through this point and zero. By a simple calculation of this kind a curve for any raw material may be obtained.

To illustrate the use of these curves for calculating the formula from the batch weights of an enamel, the same composition will be used as in illustrating the use of the preceding curves (Fig. 7). The method employed is the same. Following the horizontal line corresponding to the weight of a material to the right until it intersects the curve for one of the oxides obtained from the substance, and dropping vertically to the base of the diagram, the corresponding molecular proportion of that oxide is obtained.

**Molecular Parts of Oxides**

| Material | Weight | $K_2O$ | $Na_2O$ | CaO | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ | F | $SnO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Feldspar | 178 | 0.32 | ..... | ..... | 0.32 | 1.92 | ..... | ..... | ..... |
| Flint | 140 | ..... | ..... | ..... | ..... | 2.344 | ..... | ..... | ..... |
| Borax | 83 | ..... | 0.219 | ..... | ..... | ..... | 0.438 | ..... | ..... |
| Soda ash | 15 | ..... | .142 | ..... | ..... | ..... | ..... | ..... | ..... |
| Saltpeter | 16 | .08 | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| Fluorspar | 10.5 | ..... | ..... | 0.136 | ..... | ..... | ..... | 0.27 | ..... |
| Cryolite | 59.5 | ..... | .426 | ..... | .142 | ..... | ..... | 1.70 | ..... |
| Tin oxide | 34 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 0.225 |
| Total | ..... | .40 | .787 | .136 | .462 | 4.264 | .438 | 1.97 | .225 |
| | | | 1.323 | | | | | | |
| Dividing by 1.323 | ..... | .320 | .595 | .103 | .349 | 3.223 | .331 | 1.49 | .170 |

The empirical formula is then written

$$\left.\begin{matrix} 0.302\ K_2O \\ .595\ Na_2O \\ .103\ CaO \end{matrix}\right\}\ 0.349\ Al_2O_3 \left\{\begin{matrix} 3.223\ SiO_2 \\ .331\ B_2O_3 \\ .170\ SnO_2 \\ 1.490\ F \end{matrix}\right.$$

In order to facilitate the reading of these curves, as in the preceding set, it is sometimes necessary to use larger quantities than

those given in the batch. The weight given is multiplied by a convenient factor, which is, of course, used as a divisor of the quantity of oxide obtained from the curve.

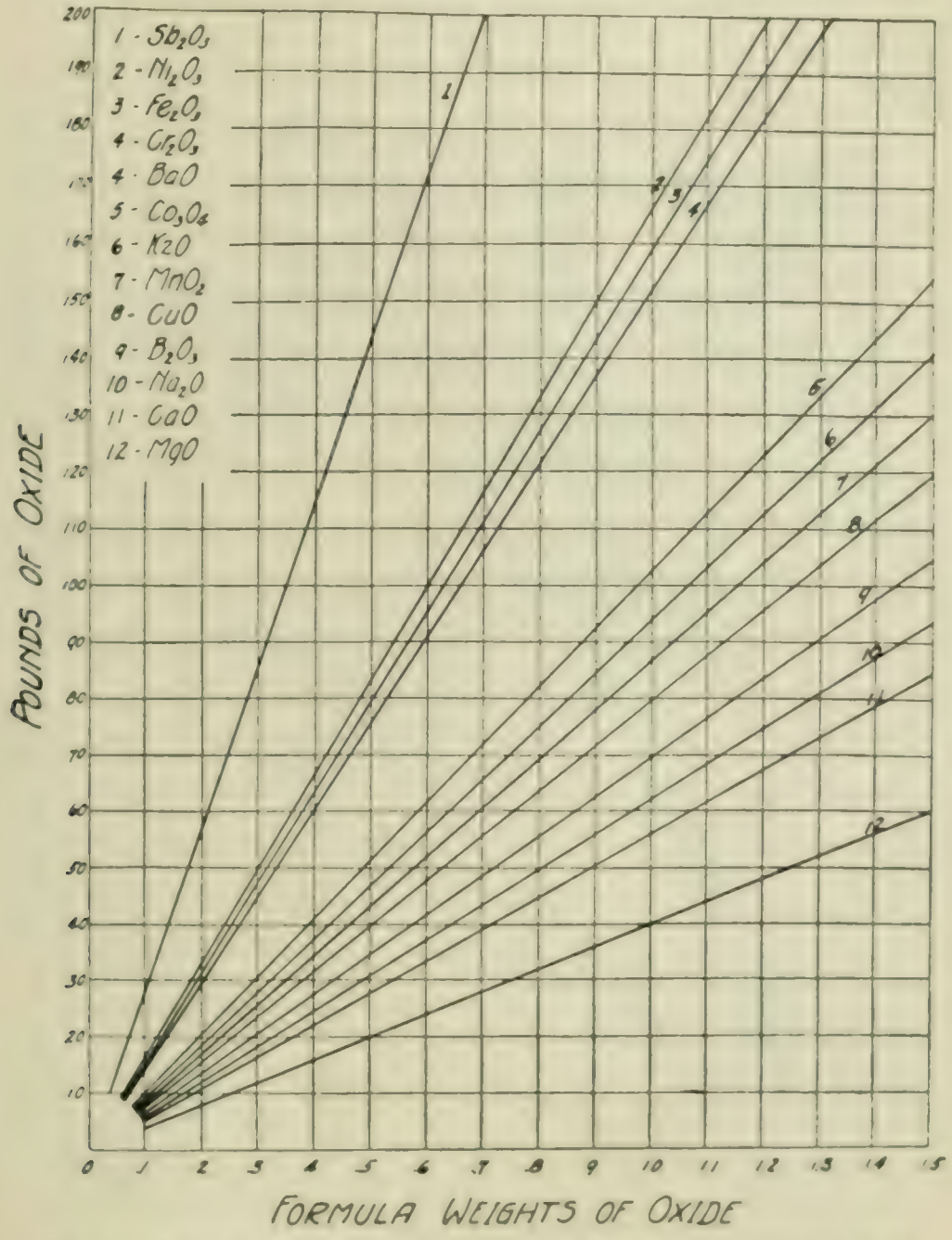


FIG. 8.—*Chart for obtaining formula weights of oxide from pounds of oxide*

The molecular proportions of the oxides obtained from the batch weights are divided, as in preceding calculations, by the sum of the values for the basic or RO oxides, to get the formula in standard form, unit RO.

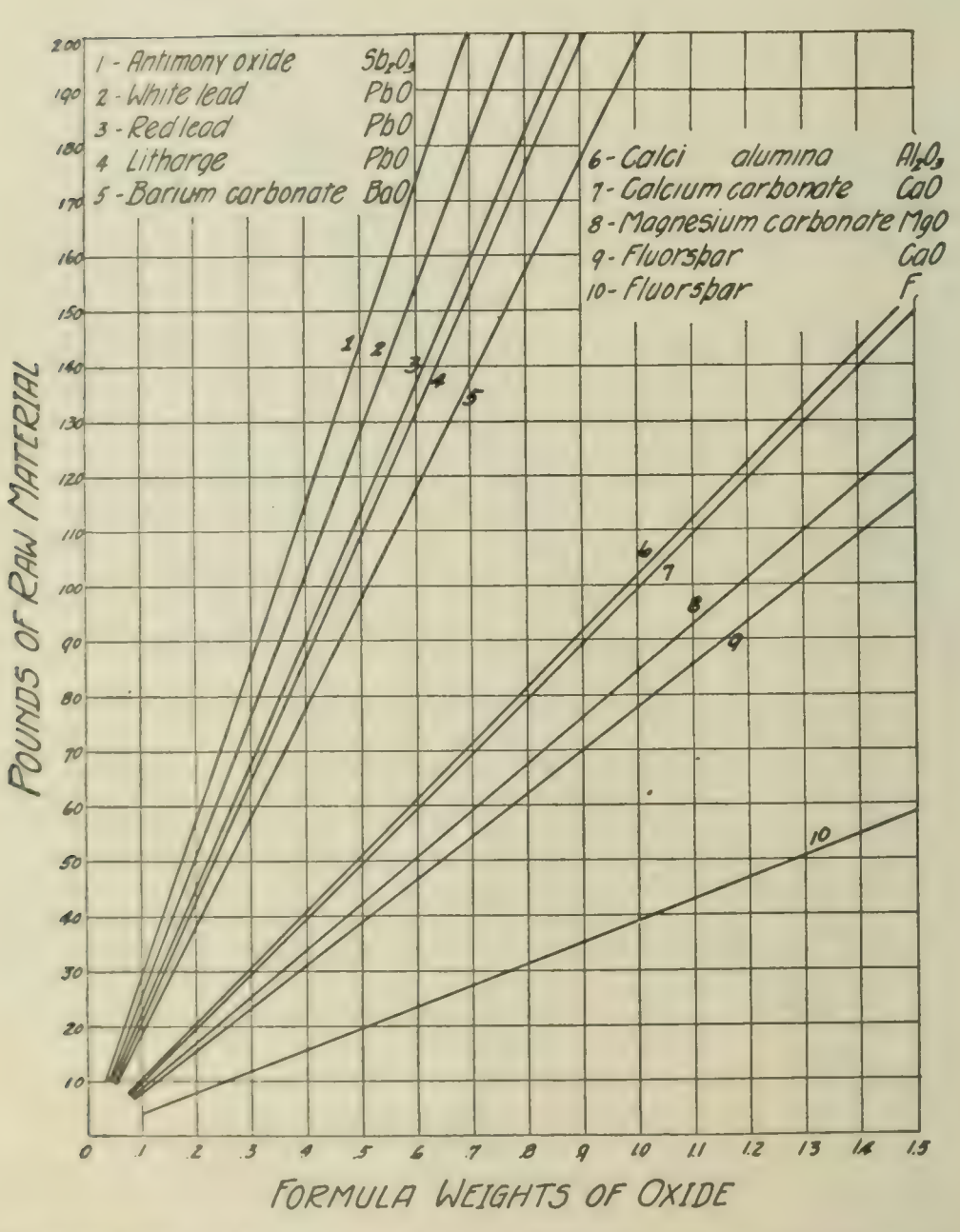
1 - Antimony oxide $Sb_2O_3$
2 - White lead PbO
3 - Red lead PbO
4 Litharge PbO
5 - Barium carbonate BaO
6 - Calci alumina $Al_2O_3$
7 - Calcium carbonate CaO
8 - Magnesium carbonate MgO
9 - Fluorspar CaO
10 - Fluorspar F
POUNDS OF RAW MATERIAL
FORMULA WEIGHTS OF OXIDE
0 .1 .2 .3 .4 .5 .6 .7 .8 .9 1.0 1.1 1.2 1.3 1.4 1.5
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

FIG. 9.—*Chart for obtaining formula weights of oxide from pounds of raw material*

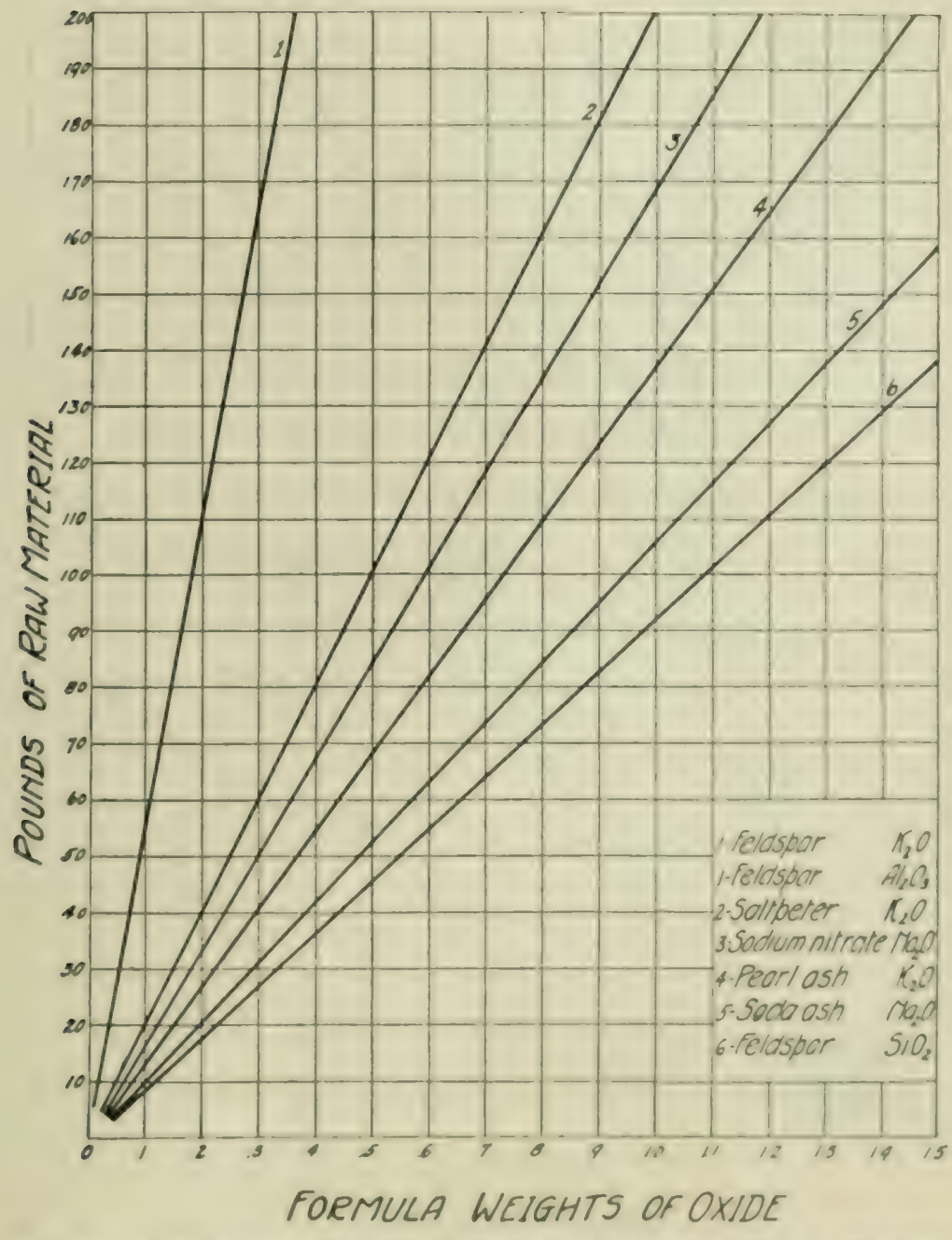


FIG. 10.—*Chart for obtaining formula weights of oxide from pounds of raw material*

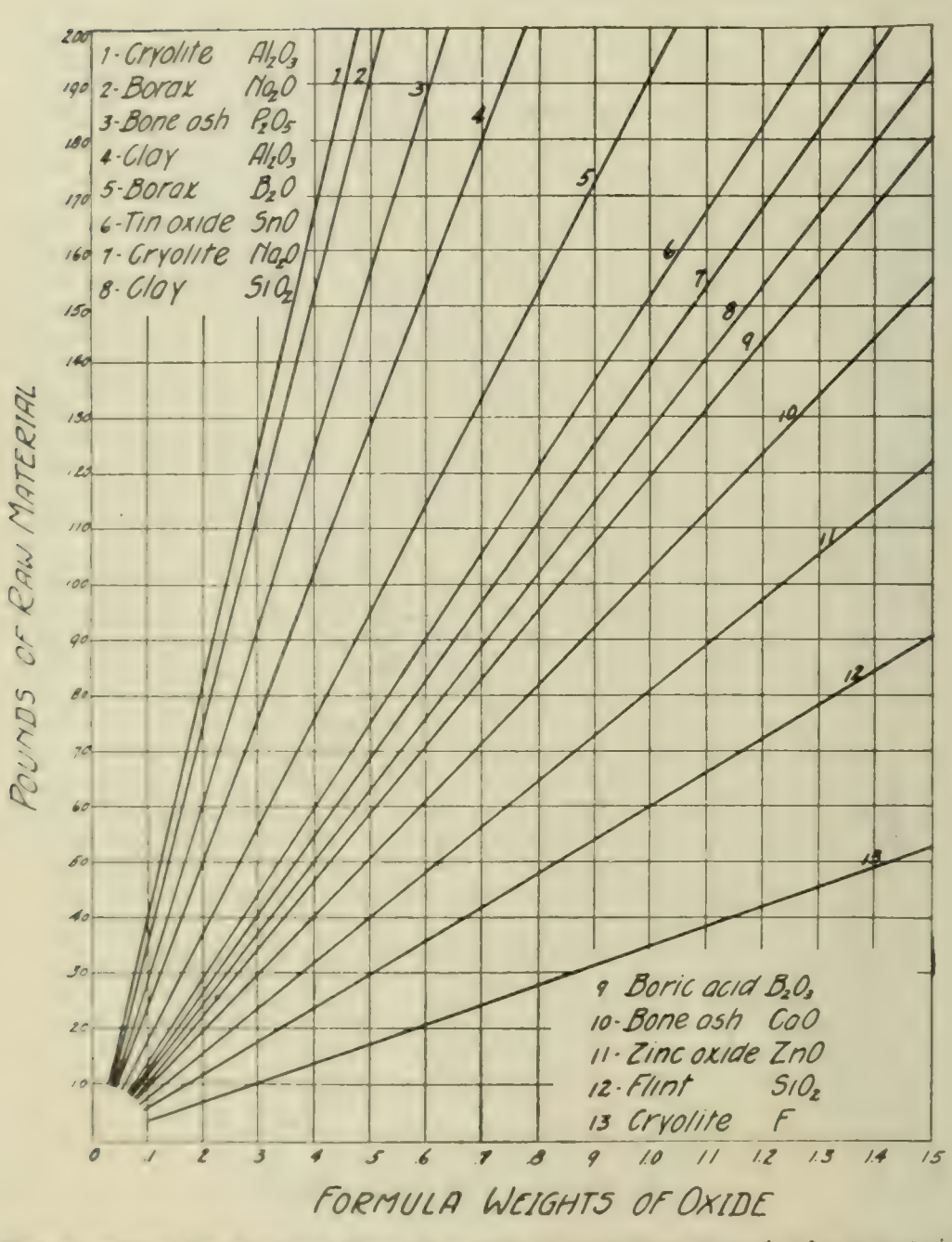


FIG. 11.—*Chart for obtaining formula weights of oxide from pounds of raw material*

## VII. PHYSICAL PROPERTIES OF ENAMELS

### 1. INTRODUCTION

Articles are made of enameled iron for a great variety of purposes. In all cases it is the function of the enamel to protect the iron from corrosion. This may be its only function, as, for instance, in the case of enameled-steel articles for chemical purposes, where all other considerations are of negligible importance. On the other hand, the enamel sometimes has to perform the double function of protecting the iron from corrosion and imparting a desirable surface to the ware while subjected to treatment which has a strong tendency to destroy it. Enameled-iron cooking utensils fall in this class. A piece of ware used in the kitchen must withstand the solvent action of hot solutions, sometimes acid, sometimes alkaline, and the average housewife will soon discard it after it acquires a soiled appearance which she can not remove with scouring soap.

Another class of ware is that in which the chief function of the enamel is to impart a desired finish to the surface. In this class, while the enamel does necessarily protect the iron from corrosion, the ware is not subjected to such strong corroding agencies as in the two classes given above. As representative of this class may be mentioned reflectors and advertising signs.

The function of the iron in all cases is to serve as a support for the enamel. The primary object in making enameled-iron articles is to obtain a very strong article with little weight, such as is obtained with steel, but having surface properties such as are exhibited by glass. It is evident, therefore, that an enamel for any given purpose must possess physical properties which will enable it to withstand the destructive action of the agencies with which it comes in contact. These physical properties of the enamel are, like those of glass, influenced very greatly by its ultimate chemical composition; but there are many other factors vitally affecting the quality of the enameled ware.

### 2. RESISTANCE TO SUDDEN CHANGE OF TEMPERATURE

The ability of enamel to withstand sudden changes of temperature is one of the important properties of enameled wares. The ordinary enameled pan is continually subjected to hard usage in the kitchen, such as boiling dry and immediately running cold water into it.

Professor Staley in his very excellent article on "Cause and Control of Crazing in Enamels on Cast Iron"[19] says:

> Three coördinate factors must always be acting to affect the fit of an enamel coat on an iron casting: (1) Difference in coefficient of contraction and expansion of the iron and enamel; (2) the strength of the enamel, which is largely dependent upon proper attachment to the iron; (3) elasticity (ductility) of the enamel, which is largely dependent upon a thin and uniform coat.

With these statements the writer is in full accord. They apply equally well to cast-iron and steel enamels.

The first of these three factors is quite generally recognized and is ordinarily thought to be the most important factor governing the toughness of enamel. The last two are equally important. Every enameler knows that a thin enamel will stand far more rough treatment than a heavy one. A piece of thin steel with a thin coat of enamel can be bent through a comparatively sharp angle and straightened out again without any rupture of the enamel visible to the naked eye. Imagine a sheet of glass, of even the same thickness as the enamel, receiving the same treatment. It will break before it has bent through any perceptible arc. Whence this difference? It lies in the ductility (elasticity) of the enamel coating and the support given by the steel base. This great elasticity, together with high tensile strength of the enamel coating, resulting from the combined tensile strength of the frit and its strong bond to the steel, is the most important factor in producing tough enamels and ware which stands severe treatment, such as abrasion and sudden changes in temperature.

Winkelmann and Schott's[20] investigations throw some light on the relation between chemical composition and physical properties of glass. Table 5 shows some of the values determined for different oxides, expressing their relative effect upon the physical properties.

The glasses from which these values were determined were of much more simple composition than the average enamel. It is not certain, therefore, how well the factors would apply to enamels. They do have value, however, in indicating the relative effects of the different oxides on specific physical properties, and a general idea may be obtained as to what oxides are most efficient in producing a desired physical property. It may be noted in this connection that glasses of high density show high luster. The figure for $B_2O_3$ is an exception in this respect when applied

[19] Staley, H. F., Trans. Am. Ceram. Soc. **14**, p. 530; 1912.
[20] Hovestadt, Jena Glass.

to enamels. The effects of the various oxides on tenacity and elasticity is worthy of note in connection with enamel compositions.

**TABLE 5.—Coefficients for Mechanical Properties of Glasses**

| | Density | Coefficient of elasticity[a] | Crushing strength | Tensile strength |
|---|---|---|---|---|
| $SiO_2$ | 2.3 | 70 | 1.23 | 0.09 |
| $B_2O_3$ | 1.9 | 80 | .90 | .05 |
| ZnO | 5.9 | 100 | .60 | .15 |
| PbO | 9.6 | ..... | .48 | .025 |
| BaO | 7.0 | 70 | .05 | .05 |
| CaO | 3.3 | 70 | .20 | .20 |
| MgO | 3.8 | 40 | 1.10 | .01 |
| $K_2O$ | 2.8 | 70 | .05 | .01 |
| $Na_2O$ | 2.6 | 100 | .02 | .02 |
| $Al_2O_3$ | 4.1 | 150 | 1.00 | .05 |
| $P_2O_5$ | 2.55 | ..... | .76 | .075 |
| $As_2O_5$ | 4.1 | 40 | 1.00 | .03 |

[a] Factors for borosilicate glasses free from PbO and $P_2O_5$.

By use of these factors values were calculated for glasses by the formulas

$$\frac{100}{S} = \frac{a_1}{z_1} + \frac{a_2}{z_2} + \frac{a_3}{z_3} + \cdots$$

$$E = a_1x_1 + a_2x_2 + a_3x_3 + \cdots$$

$$P = a_1y_1 + a_2y_2 + a_3y_3 + \cdots$$

$S$ = specific gravity of the glass;

$E$ = coefficient of elasticity of the glass;

$P$ = tensile or crushing strength of the glass;

$a_1a_2a_3$ = percentages of various oxides in the glass;

$z_1z_2z_3$ = density factors for various oxides;

$x_1x_2x_3$ = coefficient of elasticity factors;

$y_1y_2y_3$ = tensile or crushing strength factors.

### 3. RESISTANCE TO ABRASION

The ability of enamels to withstand abrasion depends largely upon the same properties as their ability to stand sudden changes in temperature. If enamels are so constituted as to be able to stand the latter they will probably also stand the former. Recapitulating, we may say that toughness is imparted to enamel by (1) proper union of the enamel to the steel and proper union of the different coats of enamel, (2) the use of as thin a coating of enamel as circumstances will permit, (3) making the frit of such a composition as to have high elasticity and tensile strength.

### 4. CONTROLLING THE TOUGHNESS OF ENAMELS

Toughness, as applied to steel or sheet-iron enamels, is understood to mean the ability to withstand impact or flexure. (1) The first and most important precaution to take in controlling this property is to *keep all enamels thin.* (2) The heavier the steel the tougher the ware. (3) Places where there is double thickness of steel due to lapping parts riveted or welded on necessitate special care in dipping and burning. A thinner or more fusible enamel on such parts, where practicable, makes for better quality. (4) Sharp angles should be avoided. (5) Do not grind enamel too finely. Ground coat especially should be quite gritty when applied; 60-mesh is fine enough, 100-mesh is too fine. (6) Overburning is better than underburning; either will destroy toughness if carried to extremes. (7) Sudden cooling by exposure to draft of air or setting ware on cold surface makes brittle ware. (8) Metallic oxides add toughness to enamel, especially $Co_3O_4$, $Ni_2O_3$, CuO, $MnO_2$, PbO, and $Fe_2O_3$. (9) The formula of the enamel should be well balanced in all respects, due regard being paid to those articles which add elasticity and tensile strength. In reference to this it must be remembered the elasticity and toughness of the finished product are influenced quite as much by the manipulation of the enamel as by its composition. ZnO, $Al_2O_3$, $SiO_2$, CaO, BaO, and $B_2O_3$ all are valuable ingredients, but the properties of the enamel depend far more upon the ratios between them than upon the influence of any one individually. (10) Use caution in adding raw material at the mill. A little magnesia is good; 6 to 10 per cent clay is sufficient. A little raw flint sometimes is valuable. (11) Fluorides are undesirable. In large amounts they make poor enamels. A white enamel depending largely on fluorides for opacity is very likely to be of poor quality so far as toughness is concerned. (12) Strict attention to every detail in the process of manufacture is absolutely essential.

## VIII. RESISTANCE OF ENAMELS TO CHEMICAL ACTION

### 1. INTRODUCTION

The ability of enamels to resist corrosion by the chemical action of water and of solutions which come in contact with them depends primarily upon the ultimate chemical composition of the surface exposed to these solvents, but of no less importance is the degree to which the material approaches a homogeneous glass. The higher the percentage of unfritted materials added to the enamel, the greater the danger of destruction by chemical action.

Enamels for sheet steel are generally applied by dipping or spraying, and this requires the addition of certain raw materials to the frit in order to get the enamel properly applied. White enamels require an addition of an opacifier, such as tin oxide or a substitute, in addition to raw clay for floating the frit, and a flocculating agent, such as borax or other salts. In view of the fact that these enamels are burned in from two to four minutes, it is very evident that complete chemical union of these raw materials with the frit can not be obtained. It follows, therefore, that the finished enamel is always composed of the frit carrying in suspension either the raw material as added or some compound of the frit with the raw material, representing a partially completed reaction and a conglomerate mixture of materials, far from homogeneous and very unlike a clear glass, such as glass vessels are made of.

### 2. ACTION OF GLASS

Experiments performed by Schott, Foerster, and Mylius [21] have shown how susceptible even high-grade glass is to the chemical action of water. They show that the solvent action does not proceed directly, as water dissolves sugar, but that the glass surface absorbs water from the air or solution in contact with it. The process of solution, resulting in the passage from solid glass to dissolved substance, is affected through a series of intermediate transformations. They note that water glass and other glasses containing little lime are especially susceptible to this solvent action. This citation emphasizes the importance not only of the ultimate chemical composition, but also of the thoroughness with which the enamel is melted to a homogeneous mixture. It is obvious that soluble salts and especially alkalies should not be added in large amounts in the mill if enamels are to be subjected to destructive chemical agencies.

Foerster's conclusions, as a result of experiments on the solubility of many types of glass, are summarized as follows:

1. The total alkalies in glass have a marked effect upon its power to resist corrosion by water.

2. In good glasses it is immaterial whether potash or soda is the source of the alkali.

3. Boric acid in combination with silicic acid seems to check solution.

Kohlrausch [22] tested a number of glasses for solubility in water and concluded that solubility is mainly determined by the gross

[21] Hovestadt, Jena Glass, p. 130 [22] Hovestadt, Jena Glass, p. 149

content of alkali. Potash, however, appeared more conducive to solubility than soda.

Walker and Smither [23] have recently made solubility tests on various brands of chemical glasswares. The analyses of the glasses are shown in Table 6.

TABLE 6—ANALYSES OF CHEMICAL GLASSWARE

| Ware | Kavalier beaker | M. E. G. Co. beaker | Pyrex beaker | Jena beaker | Jena flask | Nonsol beaker | Fry beaker | Libbey beaker |
|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 0.14 | 1.0 | 2.0 | 4.2 | 4.2 | 2.5 | 2.7 | 2.1 |
| $Fe_2O_3$ | 0.08 | 0.35 | 0.25 | 0.25 | 0.27 | 0.23 | 0.22 | 0.44 |
| ZnO | ..... | 5.6 | ..... | 10.9 | 10.9 | 7.8 | 3.6 | ..... |
| PbO | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 1.0 |
| MnO | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.03 | 0.03 |
| CaO | 8.7 | 0.66 | 0.29 | 0.63 | 0.56 | 0.79 | 2.6 | 0.42 |
| MgO | 0.17 | 4.3 | 0.06 | 0.21 | 0.25 | 3.4 | 2.6 | 0.08 |
| $Na_2O$ | 7.1 | 10.8 | 4.4 | 7.5 | 7.8 | 10.9 | 9.8 | 8.2 |
| $K_2O$ | 7.9 | 0.30 | 0.20 | 0.37 | 0.31 | 0.30 | 1.5 | 0.67 |
| $SiO_2$ | 75.9 | 73.0 | 80.5 | 64.7 | 64.7 | 67.3 | 68.6 | 75.9 |
| $B_2O_3$ | ..... | 3.6 | 11.8 | 10.9 | 10.6 | 6.2 | 8.1 | 10.8 |
| $P_2O_5$ | 0.08 | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| $SO_3$ | 0.20 | 0.02 | ..... | ..... | ..... | ..... | ..... | ..... |
| $As_2O_3$ | Trace | 0.02 | 0.70 | 0.14 | 0.19 | Trace | 0.18 | 0.36 |
| $Sb_2O_3$ | ..... | 0.60 | ..... | ..... | ..... | 0.62 | ..... | ..... |
| Total | 100.29 | 100.27 | 100.21 | 99.81 | 99.79 | 100.05 | 99.93 | 100.00 |

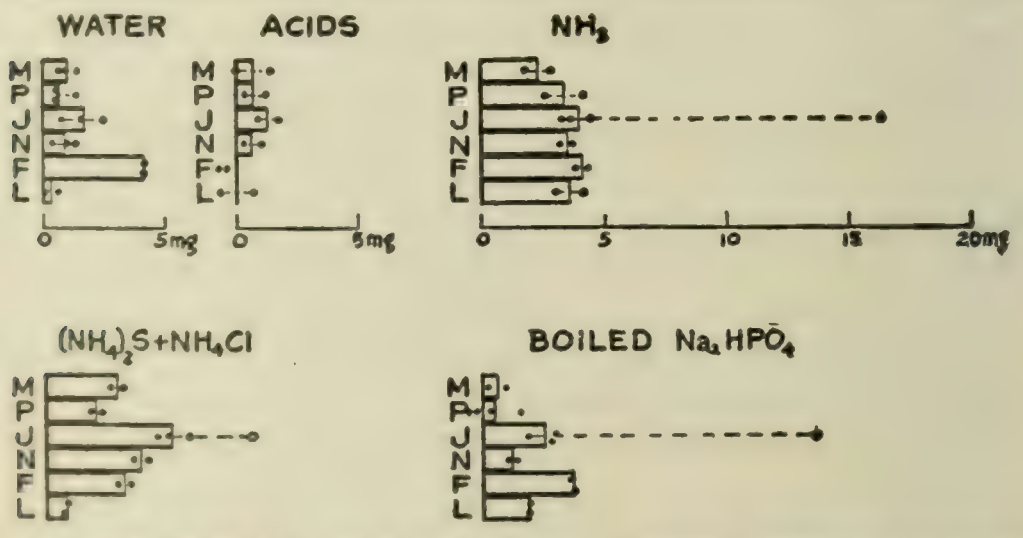


FIG. 12.—*Loss in weight of flasks with water, acids, ammonia, ammonium sulphide and chloride, and sodium-phosphate solutions*

The glasses were subjected to the action of boiling water and various acid and alkaline solutions, and the loss of weight was determined with care.

The results are shown in Figs. 12 and 13, in which the letters *K*, *M*, *P*, *J*, *N*, *F*, and *L* indicate Kavalier, M. E. G. Co., Pyrex, Jena, Nonsol, Fry, and Libbey,

[23] B. S. Tech. Paper No. 12, Comparative Tests of Chemical Glassware.

respectively. In these figures individual accepted determinations are shown by dots; determinations which are believed in error, and therefore omitted from the averages, are indicated by circles. The length of the rectangles indicates averages of the accepted values.

Cowper,[24] who noted that solutions of ammonium sulphide and chloride attacked glass more vigorously than sodium carbonate, must have used glass very different from the ware tested here.

Table 7 gives a general summary of the resistance to the various solutions and to mechanical and heat shocks of the wares tested. In this table the numerical

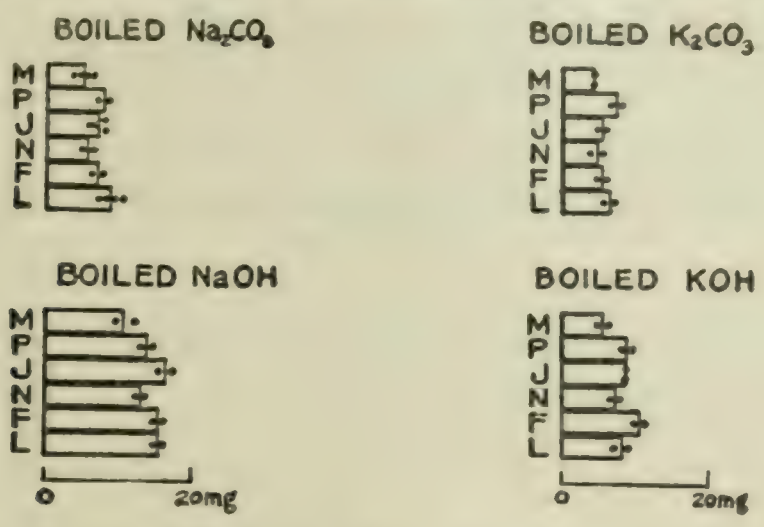


FIG. 13.—*Loss in weight of flasks with sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide solutions*

subscripts indicate the minor differences in resistance, the lowest number being the most resistant. The absence of a subscript indicates that the differences in resistance are too small to justify any differentiation between the wares graded in the same group. In the rating of resistance to caustic alkalies the boiling tests only have been considered.

TABLE 7

| Ware | Resistance to | | | | | | |
|---|---|---|---|---|---|---|---|
| | Water | Mineral acids | Carbonated alkalies | Caustic alkalies | Ammonia and ammonium salts | Heat shock | Mechanical shock |
| Kavalier | Poor | Good | Poor | Good $_2$ | Good $_2$ | Poor | Poor |
| M. E. G. Co. | Good $_2$ | do | Good $_1$ | do.$_1$ | do | do | Do. |
| Pyrex | do.$_3$ | do | do.$_3$ | Fair | do | Good $_1$ | Good [a] |
| Jena | do.$_4$ | do | do.$_2$ | do | do | do.$_3$ | Fair |
| Nonsol | do.$_3$ | do | do.$_1$ | do | do | do.$_2$ | Do. |
| Fry | do.$_4$ | do | do.$_2$ | do | do | Poor | Good |
| Libbey | do.$_1$ | do | do.$_3$ | do | do | Good $_2$ | Do. |

[a] Far superior to any of the other wares.

### 3. WORK OF ORTON

Prof. Edward Orton, jr., has reported[25] the results of tests on three makes of enameled-steel automobile tags. The tags

[24] Jour. Chem. Soc., 41, p. 254, 1882.

[25] Jour. Am. Ceram. Soc., 11, pp. [illegible]

were subjected to the following chemical tests: Boiling in water for 8 hours; boiling in 1 per cent sulphuric acid for 15 minutes; exposure to acid fumes by being kept for 18 hours in a bell jar in which a beaker of strong hydrochloric acid was sitting. The relative order of resistance of the three makes of enameled ware was the same in these three tests. Boiling in dilute sulphuric acid proved the most severe test, and boiling in water the next in severity. The physical tests consisted of slow bending, repeated light impact blows, and heavy impact blows of increasing force. The order of resistance to the various tests of the three lots of enameled tags is shown in Table 8.

**TABLE 8.—Order of Resistance of Enameled Automobile Tags to Chemical and Physical Tests**

| Lot | Boiling water | Boiling dilute acid | Acid fumes | Slow bending | Light impact | Heavy impact |
|---|---|---|---|---|---|---|
| 1 | 2 | 2 | 2 | 1 | 3 | 1 |
| 2 | 1 | 1 | 1 | 3 | 1 | 3 |
| 3 | 3 | 3 | 3 | 2 | 2 | 2 |

Prof. Orton's conclusions on the results of the above tests are as follows:[26]

1. Wide differences are found in solubility, either in water, or dilute acids, or even acid fumes, between enamels of apparently equal quality.

2. No correlation can yet be shown between chemical-resisting properties and physical strength or beauty of appearance and finish. It seems as if excellence in several directions might be possessed by one and the same piece of enameled metal, but there is no causal relationship between these various kinds of excellence and it is much more likely that any single piece will be deficient in one or more directions.

### 4. WORK OF SHAW—FIRST INVESTIGATION

A study of the relation of chemical composition to the resistance to acid corrosion as well as tests to determine the resistance to sudden temperature changes was made by the writer on a large number of white enamels.[27]

The formula selected as a basis for the investigation was as follows:

$$\left.\begin{matrix} 0.4\ Na_2O \\ .2\ K_2O \\ .4\ CaO \end{matrix}\right\} x\ Al_2O_3 \left\{\begin{matrix} y\ SiO_2 \\ \\ z\ B_2O_3 \end{matrix}\right.$$

$x$, $y$, and $z$ were variables, the RO remaining constant. This RO is a little higher in CaO than the average of white enamels, but it

[26] Trans. Am. Ceram. Soc., 11, p. 155. [27] J. E. Shaw, Trans. Am. Ceram. Soc., 12, pp. 463–494

was made so in order to insure any of the enamels against solubility because of the RO. The average white enamel formula is about as follows:

$$\left.\begin{matrix} 0.5\ Na_2O \\ .2\ K_2O \\ .3\ CaO \end{matrix}\right\} 0.15\ Al_2O_3 \left\{\begin{matrix} 1.7\ SiO_2 \\ \\ .4\ B_2O_3 \end{matrix}\right.$$

Of course, there are many variations in composition which this does not include, some formulas containing $P_2O_5$, $Sb_2O_3$, PbO, BaO, and ZnO, but they are rather the exception than the rule. In the enamels tested the $SiO_2$ was varied from 1.083 to 4.53 molecular parts; the $SiO_2$-$B_2O_3$ ratio was varied from 3:1 to 7:1, and the alumina from 0.1 to 0.4 molecular parts. In all 120 compositions were made.

The test pieces used were rectangular pieces of 26-gage steel, 1½ by 3 inches. Each sample was coated on both sides with a reliable ground coat, care being taken in coating and burning to see that the edges remained coated with enamel. Seven samples were coated with each enamel, two coats of white being applied to each sample on both sides.

The time and temperature of burning were varied to suit the different enamels. Some enamels required high temperature and longer time in the muffle than others. The object was to produce the very best piece of ware that could be produced with each enamel. The temperature used for burning varied from 1500 to 1800° F, increasing with increase of $SiO_2$ and $Al_2O_3$ and decrease of $B_2O_3$.

For testing these enamels two acids were used in order to compare the results. A sample of each enamel was boiled for 15 minutes in a 1 per cent solution of $H_2SO_4$ and the operation repeated on a new sample for accuracy. Another sample of each enamel was boiled for 20 minutes in a 75 per cent solution of acetic acid and the operation repeated on a new sample.

After having weighed each sample accurately to 0.001 g, they were placed in a vessel of distilled water and the water heated to boiling. The $H_2SO_4$ solution, having been accurately measured to make a 1 per cent solution of acid, using distilled water and concentrated acid, was also heated to boiling. The samples were then taken out of the boiling water and placed in the boiling acid. This precaution was taken in order to insure no loss in weight from the enamel peeling off because of cold samples being thrown in boiling acid. As soon as the samples had boiled for 15 minutes they were placed in hot water, and cold water was run in to

insure gradual cooling. They were then thoroughly washed in distilled water by gentle rubbing with a soft cloth. After drying, they were again accurately weighed. The difference in weight represented loss due to solution. Each sample having an area of 9 square inches, the total loss divided by 9 represented the loss per square inch of exposed surface. The operation with the acetic acid was exactly the same as with the $H_2SO_4$.

Comparison of the resistance of enamels to acid treatment has at times been based on the percentage of weight lost by enameled pieces when subjected to the same acid treatment. It seems quite obvious that this basis for comparison is wrong and will lead to contradictory results. For instance, suppose we have two pieces of ware, both containing the same surface area, one of 18-gage steel with a ground coat, two coats of white, and a coat of blue, all heavy coats. The other 20-gage, but all light coats of enamel. Obviously, the latter piece will be much the lighter of the two. Now if the same enamel is used on each piece of ware, it is likely that on going through the same acid treatment the actual amount dissolved will be practically the same, but the percentage of weight lost will be quite different. Hence, it seemed that it would be more accurate to base this comparison on the absolute loss per unit of exposed area.

The following statements may be made in reference to the solubility of the enamels in sulphuric acid:

1. Everything else being constant, the solubility decreased directly as the $SiO_2$ increased.

2. Everything else being constant, the solubility decreased as the content of $Al_2O_3$ increased.

3. Everything else being constant, the solubility decreased as the $B_2O_3$ decreased.

4. The three foregoing statements may be summed up in the one—that the solubility decreased as the enamels became more refractory.

5. When the enamels became too refractory they were unusable on account of tendency to chip off and failure to develop gloss during burning.

The results of the acetic acid test were not so sharply defined as in the $H_2SO_4$ test, but in general the statements made concerning solubility in $H_2SO_4$ also hold true with regard to acetic acid. One fact was quite clearly shown; namely, 75 per cent solution of acetic acid has very much less solvent action on enamels than has a 1 per cent solution of $H_2SO_4$. This was indicated, not

only by the very low loss per square inch in weight, but by the fact that so many samples retain their gloss after the acetic acid treatment, while none of the enamels showed any gloss after $H_2SO_4$ treatment. The gloss was affected to some extent on all samples by the acetic acid, but the effect on those high in $SiO_2$ and $Al_2O_3$ was very slight indeed.

### 5. WORK OF SHAW—SECOND INVESTIGATION

(*a*) ENAMELS TESTED.—A manufacturer found that his white enamel, which was giving satisfaction when used on cooking utensils, was easily destroyed by lemon juice. The series of enamels shown in Tables 9 and 10 was made in order to produce a pure white enamel with high gloss which would not be affected. The formulas are given in the order in which the enamels were made. It is not possible to arrange the series as a whole in any logical sequence as regards composition, for the list includes variations in every ingredient of the enamel. The conditions under which the work was done precluded the possibility of covering entirely the field of possible compositions, since this was a factory problem requiring quick solution. The method of attack consisted in making up and testing a series of enamels, then preparing another series on the basis of information obtained from the first. The formulas given are for the frits only. In some cases no raw material other than clay was added. All variations in the material added at the mill are stated in discussing the results.

(*b*) RESULTS OF ACID TESTS.—Each enamel was applied to steel and then tested with lemon juice, which contains about 7 per cent citric acid, a standard 10 per cent solution of citric acid, and also a 10 per cent solution of oxalic acid. Each test consisted in washing the ware thoroughly with soap and water, drying it, and dropping the solution on the surface. The solution was left on the ware for different periods—10 minutes, 30 minutes—and some was allowed to evaporate to dryness.

Examination of the original formula shows it to be about average white enamel in all respects. This enamel was readily attacked by the lemon juice and other acid solutions. The 10-minute treatment left a distinct rough spot, while the 30-minute treatment produced a very rough spot.

Enamel 1 took a stain when treated with 10 per cent citric acid. It did not lose its gloss readily, but the iridescent stain left after two hours' treatment is characteristic of all enamels which are attacked by acid. It is the first indication of

attack, which is followed by dullness, loss of gloss, and finally rough, uneven surface. Enamel 2 lost its gloss when tested with acid.

**TABLE 9.—Formulas of Enamels**

| | $K_2O$ | $Na_2O$ | CaO | MgO | PbO | BaO | ZnO | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ | $Sb_2O_3$ | $\frac{SiO_2}{B_2O_3}$ | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Original | 0.18 | 0.59 | 0.13 | 0.0 | 0.0 | 0.05 | 0.06 | 0.26 | 1.96 | 0.48 | 0.04 | 4.0 | 1.22 |
| 1 | .04 | .36 | .20 | 0 | 0 | .20 | .20 | .10 | 3.0 | .40 | 0 | 7.5 | .88 |
| 2 | .34 | .36 | .30 | 0 | 0 | 0 | 0 | .10 | 3.0 | .40 | 0 | 7.5 | 1.28 |
| 3 | .17 | .58 | 0 | 0 | 0 | .07 | .18 | .19 | 1.75 | .30 | .07 | 5.8 | .48 |
| 4 | .27 | .65 | .08 | 0 | 0 | 0 | 0 | .20 | 1.20 | .24 | 0 | 5.0 | 1.24 |
| 5 | .30 | .30 | 0 | .13 | 0 | .13 | .13 | 0 | 2.00 | 0 | 0 | ..... | 0 |
| 6 | .30 | .30 | 0 | 0 | 0 | .20 | .20 | 0 | 2.00 | 0 | 0 | ..... | 0 |
| 7 | .13 | .57 | 0 | .30 | 0 | 0 | 0 | 0 | 1.65 | .40 | 0 | 4.1 | 0 |
| 8 | .30 | .30 | 0 | .13 | 0 | .13 | .13 | 0 | 2.0 | 0 | 0 | ..... | 0 |
| 9 | .30 | .30 | 0 | .13 | 0 | .13 | .13 | 0 | 2.0 | .10 | 0 | 20.0 | 0 |
| 10 | .30 | .30 | 0 | 0 | .13 | .13 | .13 | 0 | 2.0 | 0 | 0 | ..... | 0 |
| 11 | .30 | .43 | 0 | 0 | 0 | .13 | .13 | 0 | 2.0 | 0 | 0 | ..... | 0 |
| 12 | .30 | .40 | 0 | .03 | 0 | .13 | .13 | 0 | 2.0 | 0 | 0 | ..... | 0 |
| 13 | 0 | .31 | 0 | 0 | .28 | .14 | .25 | 0 | 1.37 | 0 | 0 | ..... | 0 |
| 14 | 0 | .40 | 0 | 0 | .45 | .16 | 0 | 0 | 1.65 | 0 | 0 | ..... | 0 |
| 15 | 0 | .32 | 0 | 0 | .18 | .13 | .36 | 0 | 1.50 | 0 | 0 | ..... | 0 |
| 16 | 0 | .35 | 0 | 0 | .15 | .22 | .27 | 0 | 1.90 | 0 | 0 | ..... | 0 |
| 17 | 0 | .48 | 0 | 0 | .09 | .20 | .24 | 0 | 1.66 | 0 | 0 | ..... | 0 |
| 18 | 0 | .35 | 0 | 0 | 0 | .22 | .43 | 0 | 1.90 | 0 | 0 | ..... | 1.08 |
| 19 | 0 | .55 | 0 | 0 | .11 | .16 | .20 | .09 | 1.27 | 0 | 0 | ..... | 1.08 |
| 20 | 0 | .60 | 0 | 0 | 0 | .10 | .10 | .09 | 1.50 | 0 | 0 | ..... | 1.20 |
| 21 | .20 | .50 | 0 | .03 | .15 | .13 | .13 | .10 | 2.00 | 0 | 0 | ..... | ..... |
| 22 | 0 | .35 | 0 | 0 | 0 | .22 | .27 | .10 | 2.00 | 0 | 0 | ..... | 1.20 |
| 23 | .30 | .40 | 0 | .03 | 0 | .13 | .13 | .14 | 2.00 | 0 | 0 | ..... | 0 |
| 24 | .30 | .40 | 0 | 0 | 0 | .15 | .15 | 0 | 3.0 | .10 | 0 | 30.0 | 0 |
| 25 | .18 | .28 | .34 | .02 | 0 | .09 | .09 | .07 | 1.46 | 0 | 0 | ..... | .68 |

Enamels 3 and 4 had no lime, but both contained cryolite. No. 3 was a good soft enamel, but was easily destroyed by citric acid. No. 4 was a poor enamel and easily destroyed by citric acid.

Enamels 5 and 6 contained no lime, no fluorine, and no boric acid. These glasses were taken from Orton's Easily Fusible Glass Without the Use of Lead of Boracic Acid.[28] Neither of these showed any mark from citric acid, but they were too refractory to use as enamels. No. 6 was most refractory. No. 7 was an easily fusible enamel containing neither fluorspar nor cryolite, but it was easily destroyed with 10 per cent citric acid. No. 8 was slightly attacked and also was quite refractory. No. 9 was made by a slight addition of boric acid to No. 5. This slight amount of $B_2O_3$ caused it to be easily destroyed by citric acid, although it showed no mark when boric acid was left out.

[28] E. Orton, jr., Trans. Am. Ceram. Soc., 5, p. 395.

**TABLE 10.—Batch Weights of Enamels**

| | Antimony oxide | Boric acid | Borax | Red lead | Zinc oxide | Barium carbonate | Magnesium carbonate | Fluorspar | Saltpeter | Soda ash | Cryolite | Flint | Feldspar |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Original | 11.5 | 0 | 91.7 | ..... | 4.9 | 9.8 | ..... | 10 | 20 | 6.4 | 33.6 | 44.4 | 103 |
| 1 | 0 | [illegible] | 76.4 | [illegible] | 16.2 | 39.4 | 0 | 15.6 | 2 | 2 | 16.8 | 152 | 39.5 |
| 2 | [illegible] | [illegible] | 76.4 | 0 | [illegible] | [illegible] | 0 | 23.4 | 62 | 2 | 16.8 | 152 | 39.5 |
| 3 | 20 | 0 | 57.3 | [illegible] | 14.6 | 13.7 | [illegible] | [illegible] | 20 | 28.6 | 16.8 | 43.2 | 86.9 |
| 4 | 0 | 0 | 46.0 | [illegible] | [illegible] | [illegible] | 0 | 6.2 | 44 | 24.3 | 37.8 | 27 | 63.2 |
| 5 | [illegible] | [illegible] | [illegible] | [illegible] | 10.5 | 25.6 | 10.9 | [illegible] | 60 | 31.8 | [illegible] | 120 | [illegible] |
| 6 | 0 | [illegible] | [illegible] | [illegible] | 16.2 | 39.4 | [illegible] | [illegible] | 60 | 31.8 | [illegible] | 120 | [illegible] |
| 7 | [illegible] | [illegible] | 76.4 | [illegible] | [illegible] | 0 | 21 | [illegible] | 26.2 | 29.2 | 0 | 99 | [illegible] |
| 8 | [illegible] | [illegible] | [illegible] | [illegible] | 10.5 | 25.6 | 10.9 | 0 | [illegible] | 31.8 | [illegible] | 120 | [illegible] |
| 9 | [illegible] | 12.4 | [illegible] | [illegible] | 10.5 | 25.6 | [illegible] | [illegible] | [illegible] | 31.8 | [illegible] | 120 | 0 |
| 10 | [illegible] | [illegible] | [illegible] | 29 | 10.5 | 25.6 | 0 | [illegible] | 60 | 31.8 | [illegible] | 120 | [illegible] |
| 11 | 0 | 0 | [illegible] | 0 | 10.5 | 25.6 | [illegible] | [illegible] | [illegible] | 45.5 | [illegible] | 120 | [illegible] |
| 12 | [illegible] | 0 | [illegible] | 0 | 10.5 | 25.6 | 2.4 | [illegible] | [illegible] | 42.4 | 0 | 120 | [illegible] |
| 13 | 0 | [illegible] | 0 | 63 | 20.5 | 27.6 | [illegible] | [illegible] | 0 | 32.8 | 0 | 82.2 | [illegible] |
| 14 | [illegible] | 0 | [illegible] | 102 | [illegible] | 31.5 | [illegible] | [illegible] | 0 | 42.4 | [illegible] | 99 | [illegible] |
| 15 | [illegible] | [illegible] | [illegible] | 41 | 29.2 | 25.6 | 0 | [illegible] | 0 | 43.9 | [illegible] | [illegible] | 0 |
| 16 | [illegible] | [illegible] | 0 | 34 | 21.8 | 43.3 | 0 | [illegible] | [illegible] | 37.0 | [illegible] | 114 | 0 |
| 17 | [illegible] | [illegible] | [illegible] | 20 | 19.4 | 39.4 | 0 | [illegible] | 0 | 50.8 | [illegible] | 100 | 0 |
| 18 | 0 | [illegible] | [illegible] | [illegible] | 34.8 | 43.3 | [illegible] | [illegible] | 0 | 37.0 | [illegible] | 114 | [illegible] |
| 19 | [illegible] | [illegible] | [illegible] | 24 | 16.2 | 31.5 | [illegible] | 0 | 0 | 29.7 | 37.8 | 76.2 | [illegible] |
| 20 | [illegible] | [illegible] | 0 | 0 | 8.1 | 19.7 | [illegible] | 0 | [illegible] | 35.0 | 37.8 | 90 | [illegible] |
| 21 | 0 | 0 | [illegible] | 34 | 10.5 | 25.6 | [illegible] | 0 | 40 | 21.0 | 42 | 120 | [illegible] |
| 22 | 0 | 0 | [illegible] | 0 | 21.8 | 43.3 | [illegible] | [illegible] | [illegible] | 5.3 | 42 | 120 | [illegible] |
| 23 | [illegible] | 0 | 0 | [illegible] | 10.5 | 25.6 | 2.4 | 0 | 52 | 38. | 0 | 63.6 | 79 |
| 24 | [illegible] | 0 | 19.0 | [illegible] | 12.1 | 29.5 | [illegible] | [illegible] | [illegible] | 37.4 | 0 | 180 | [illegible] |
| 25 | [illegible] | [illegible] | [illegible] | [illegible] | 7.3 | 17.7 | 1.7 | 26.5 | 30 | 27.5 | 0 | 60 | 39.5 |

No. 10 was made by substituting PbO for MgO in No. 5. The result was the same as when boric acid was added; the desired fusibility was obtained, but the enamel was distinctly etched by one hour's treatment with 10 per cent citric acid.

No. 11 was made by replacing the MgO in No. 5 with $Na_2O$. Distinct improvement was noted. The fusibility increased, and the enamel was not visibly affected by 10 per cent citric acid.

No. 12 was very similar to No. 11 and was practically acid-proof. This enamel was used successfully as a glass coating over another white enamel. It was too refractory to work satisfactorily alone, but it was the best enamel obtained for the desired purpose.

Enamels 13, 14, 15, 16, and 17 were further attempts to soften the enamel by the use of PbO. None of these contained any fluorspar or cryolite. No. 14 was very much like No. 13. No. 15 was a distinct improvement over No. 14, but still took a slight iridescent stain with 10 per cent citric. Nos. 16 and 17 were easily

fusible and showed only a slight iridescent stain when exposed to 10 per cent citric acid for 12 hours. They were unaffected by 25 per cent $H_2SO_4$ solution boiled for 2 hours. No. 18 was similar to No. 17 in the acid test, but it was still harder than Nos. 18 or 12.

Nos. 19 and 20 were composed of 80 per cent of Nos. 12 and 16, respectively, and 20 per cent cryolite. The resultant frits were very much softer than Nos. 12 and 16, making good enamels in this respect. Both were easily destroyed by citric acid. Nos. 12 and 16 were unaffected in the same treatment.

No. 21 had the same formula as No. 12, except that No. 21 contains fluorine, while No. 12 contains none. The 0.10 $Al_2O_3$ in No. 21 was obtained from cryolite. No. 21 was very soft (fusible) and easily destroyed by citric acid, while No. 12 was unaffected by citric acid and was quite refractory. No. 21 was very opaque, and good as an enamel but useless for the purpose desired.

No. 22 had the same formula as No. 16, except for fluorine and the addition of 0.10 $Al_2O_3$ in No. 22 being as cryolite. The result here was exactly the same as with No. 21. The fusibility and opacity of No. 22 were excellent, but it is easily destroyed by citric acid.

Nos. 23 and 24 were slight modifications of No. 12 in attempting to increase its fusibility. No gain in fusibility was obtained. Neither was affected by citric acid. No. 25 was easily destroyed by acid.

Summarizing the results of these tests, the following conclusions were drawn:

1. Fluorine is decidedly detrimental to enamels which are subject to weak acid solutions. When added to enamels as fluorspar or cryolite in large or small amounts, it renders them subject to easy attack and destruction by ordinary lemon juice.

2. Boric acid in easily fusible enamels renders them easily destroyed by weak acids, such as lemon juice, but in refractory enamels it can be used in small amounts and the enamels still maintain stability against acids. This conclusion is substantiated by the Pyrex and other chemical glasswares now on the market.

3. No enamel of the borosilicate type made in this series was found proof against 10 per cent citric acid.

4. Enamels containing no fluorine or boric acid can be easily made proof against citric acid, but it was not found possible to

reduce their refractoriness to a sufficiently low point to make them satisfactory as white enamels. No. 12 was the best enamel made as far as stability against lemon juice is concerned. This is too refractory to work well as a white enamel. It can be successfully applied over a hard white enamel of inferior acid resisting properties to give the desired result.

(*c*) Opaque Enamels versus Translucent Enamels.—Upon reading the results of the above, one is likely to arrive at the conclusion that enamels sufficiently fusible to burn as enamels will be readily attacked by citric acid. While this is true of the above enamels, it must be borne in mind that these enamels were all required to be white. All first-coat enamels for sheet steel are colored blue, brown, or black, and when white enamels are applied over them the heat treatment in burning must not be too severe. White enamels of the type ordinarily used for cooking utensils will be converted to a dark gray, or even black, if the burning is sufficiently prolonged. It will be seen, therefore, that the burning of white enamels is necessarily limited to a comparatively light heat treatment. Some of the enamels given above would make very good ware if it were possible to give them sufficient heat treatment to burn them well on the ware. But if they are burned to this extent, the ware would not be white. Experience has shown that enamels which are much more refractory than any of these can be burned on steel to give a very satisfactory ware, but in no case is an enamel made white by the use of opacifiers used for highly acid-resisting ware. The results obtained in this work form a very strong argument against opaque enamels and in favor of translucent colored enamels for culinary purposes or any other use where resistance to corrosion is of importance. The same thing is true of enamels required to possess toughness to a high degree, in view of the fact that colored enamels can be made in a thin coat, while white enamel coatings must be much heavier in order to be opaque.

### 6. WORK OF LANDRUM

R. D. Landrum [29] gives the result of tests on 10 white enamels for sheet steel. Various tests were made on these, including corrosion by 20 per cent acetic acid, study of behavior during rapid expansion and contraction, brittleness, elasticity, and adhesion of enamel to the iron. The accompanying table shows a summary of the data obtained.

[29] Trans. Am. Ceram. Soc., 14, p. 452.

**TABLE 11.—Results of Tests of 10 White Enamels**

| No. | Formula weights of $SiO_2$ | Molecular ratio $SiO_2$: $B_2O_3$ | Total alkalies, formula weights | Fluorine, formula weights | Order of solution | Sudden change of temperature | Resistance to impact |
|---|---|---|---|---|---|---|---|
| 2 | 1.636 | 4.1 | 0.694 | 0 | 1 | 1 | 3 |
| 3 | 2.217 | 3.5 | .991 | 0 | 2 | 3 | 9 |
| 4 | 2.571 | 9.5 | .932 | 0.721 | 3 | 10 | 6 |
| 5 | 2.447 | 8.6 | .680 | .636 | 4 | 6 | 2 |
| 1 | 2.513 | 9.6 | .683 | .599 | 5 | 2 | 5 |
| 10 | 2.013 | 3.2 | .983 | 0 | 6 | 5 | 7 |
| 9 | 2.406 | 7.4 | .732 | .834 | 7 | 8 | 10 |
| 6 | 1.558 | 3.8 | .757 | .452 | 8 | 7 | 8 |
| 7 | 2.525 | 9.9 | .679 | .598 | 9 | 9 | 4 |
| 8 | 1.509 | 3.3 | .772 | .215 | 10 | 4 | 1 |

Study of these data leads to the following conclusions regarding the action of these enamels in resisting corrosion by acetic acid:

1. Molecular amount of total alkalies does not materially affect the relative solubility of enamels. Indeed, with the exception of No. 2, the best enamel of the 10 is the one highest in total alkalies, the second best having 0.932 total alkalies.

2. The best enamels have no fluorine but high $B_2O_3$. Two of the poorest have high $B_2O_3$ and low fluorine. The presence of fluorine is distinctly detrimental to the stability of the enamel, as is evidenced by Nos. 4, 5, and 6, which should be decidedly superior to 1 and 2 because of their lower content of $B_2O_3$ and smaller content of alkalies. No. 10 is the only member of the series which does not support this conclusion. There is nothing in the composition to indicate that this enamel should not be classed with No. 3, which is very similar to it.

3. From the author's description of the fritting and color of the enamels it seems reasonable to infer that practically all of the fluorine was driven out of 4 and 5, which lends support to the conclusion that those lowest in fluorine gave best results in the acid test, irrespective of the alkali or boric acid content.

It will be observed that there is absolutely no parallelism between chemical and physical excellence. The ability of the enamel to withstand chemical corrosion seems to bear no relation whatever to its ability to withstand impact or sudden change of temperature. A still more striking fact is that there seems to be no relation between the ability of the enamels to withstand sudden change of temperature and that to withstand impact.

### 7. ACTION OF VARIOUS ACIDS ON ENAMELS

The relative action on a given enamel of different acids and of various strengths of the same acid has been the subject of considerable investigation. Landrum [30] placed a given amount of solutions of acetic acid of various strengths in vessels of a given size and coated with the same enamel. The solutions were then evaporated to dryness on a gas hot plate. The maximum action was found to occur at about 20 per cent, by volume, of acetic acid with two enamels. The action of highly concentrated acids was almost negligible. As pointed out by Staley [31], this is to be expected, for with this acid and method of testing the rate of solution of necessity varied according to the following factors:

1. THE DISSOCIATION OF THE ACID.—In dilute solutions the acid is more highly dissociated than in concentrated solutions.

2. THE AMOUNT OF ACID PRESENT.—Dilute solutions contain fewer units of acid.

3. THE RATE OF EVAPORATION.—The concentration of the acid solutions varied continuously as they were boiled, the water being evaporated first and the acid solution becoming more and more concentrated. Therefore, the more dilute the acid the longer the time during which active concentrations were acting. It also follows that the slower the rate at which the acid is concentrated the greater will be its solvent action.

Poste [32] has tested the relative action of various strengths of acetic, hydrochloric, nitric, and sulphuric acids on grains of enamel. In his first investigation he used grains passing a certain size sieve gauze. In the second he used accurately sized grains in order to avoid differences in action due to increase of surface area with increased size of grains. The results obtained were similar to those of Landrum. All the acids had their greatest solvent action at concentrations between 10 and 30 per cent.

Frost [33] conducted tests on finished enamel surfaces, following the method of Landrum. He obtained results that checked those of Landrum. The results obtained by Landrum and Frost are shown in Fig. 14.

---

[30] R. D. Landrum, Trans. Am. Ceram. Soc., 13, pp. 424-451.
[31] H. F. Staley, Trans. Am. Ceram. Soc., 13, p. 429.
[32] E. P. Poste, Trans. Am. Ceram. Soc., 17, pp. 137-149, and 18, pp. 762-766.
[33] Leon J. Frost, Jour. Am. Ceram. Soc., 1, p. 422.

In a third investigation Poste [34] studied the action of acetic, citric, and tartaric acids on grains of enamel. He found that the latter two acids were superior to acetic for testing the acid resist-

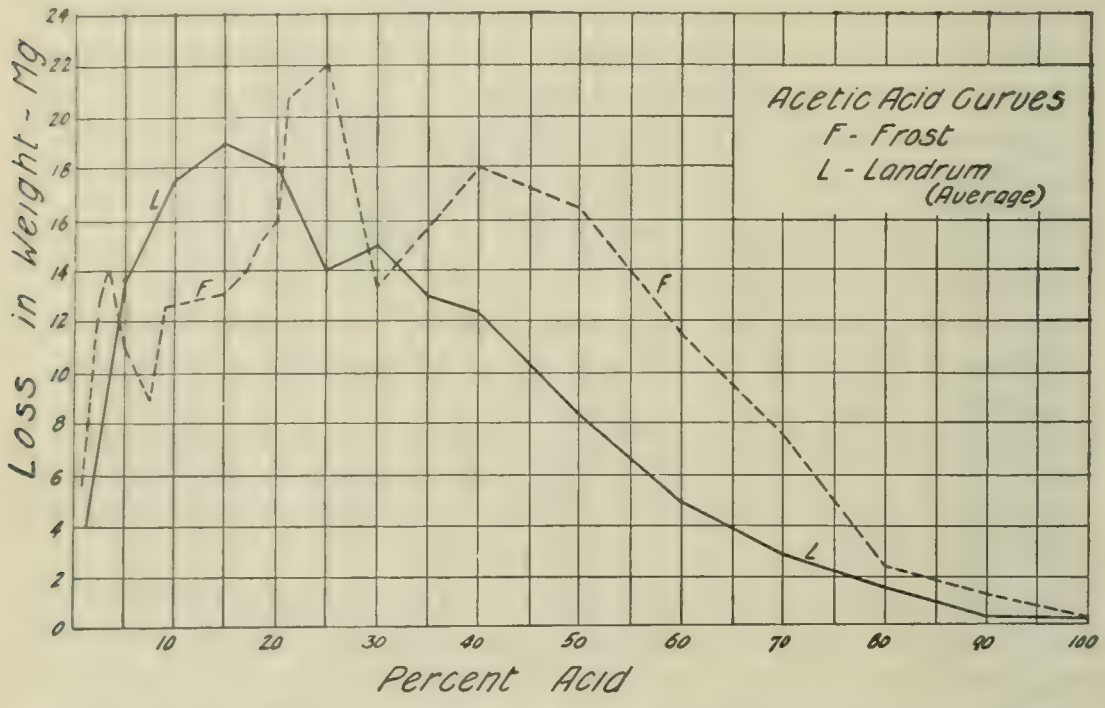


FIG. 14.—*Loss in weight of enamels with acetic acid solutions of various strengths*

ance of enamels, since the resistance does not vary much with concentrations in the region close to 20 per cent of acid.

WASHINGTON, November 11, 1919.

[34] E. P. Poste, Jour. Am. Ceram. Soc., 2, pp. 32–43.

# A CLASSIFICATION OF SHEET STEEL ENAMELS[1]



R. R. Danielson[2]

In this paper are given the compositions of typical enamels applied to sheet steel together with reasons for their use. It has not been intended to cover the field of possible composition but it has been the purpose of the writer to present proven compositions which yield several kinds of commercial enamels and enable the makers of enamels to compare them with their own.

The mill additions for gray ware enamels, shown in Table 1, consist of some high grade ball clay and magnesium carbonate. Small amounts (approximately 0.25 per cent) of some electrolyte such as magnesium sulphate or cobalt and nickel sulphates are added to the milled enamel to temper it for dipping purposes and also to promote mottling.

Ground coat enamels, A, B, and C, shown in Table 2, show a decided decrease in refractoriness from A to C and are typical of those used on various classes of enameled sheet steel ware.

In milling ground coats it is general practice to add clay and water to the frit at the beginning of the milling operation and to add the borax in a hot solution about one-half hour preceding the end of the operation.

---

[1]Abstract of a paper presented before the American Ceramic Society at the Chemical Exposition, New York, Sept. 24, 1920.
[2]Associate Enameled Metal Technologist.

Table 1.- Gray Ware Enamels

Batch Compositions of Frits

| | A | B | C |
|---|---|---|---|
| Feldspar | 30.0 | 40.0 | 43 |
| Borax | 28.5 | 30.5 | 40 |
| Quartz | 19.0 | 10.0 | -- |
| Soda ash | 8.0 | 6.5 | 5.0 |
| Sodium nitrate | 4.0 | 5.5 | 4.0 |
| Fluorspar | 3.0 | 1.5 | -- |
| Bone ash | 5.0 | 4.5 | 3.5 |
| Antimony oxide | 2.5 | 1.5 | 1.5 |
| Total | 100.0 | 100.0 | 100.0 |

Mill Batch:- Frit, 100.0; clay, 6.0; magnesium carbonate, 0.25; water, 50.0.

Table 2.- Ground Coats

Batch Compositions of Frits

| | A | B | C |
|---|---|---|---|
| Borax | 30.0 | 30.0 | 39.5 |
| Feldspar | 22.0 | 27.0 | 20.5 |
| Quartz | 29.0 | 20.5 | 22.5 |
| Soda ash | 5.0 | 9.8 | 5.0 |
| Soda nitre | 4.6 | 5.0 | 4.7 |
| Fluorspar | 6.0 | 6.0 | 6.0 |
| Cobalt oxide | 0.4 | 0.5 | 0.4 |
| Manganese oxide | 3.0 | 1.3 | 1.0 |
| Nickel oxide | 1.0 | -- | 0.4 |
| Total | 100.0 | 100.0 | 100.0 |

Mill Batch:- Frit, 100.0; clay, 7.0; borax, 1.5; water, 50.0.

93

Table 3 White Cover Enamels

Batch Compositions of Frits

| | A | B | C |
|---|---|---|---|
| Borax | 38.0 | 27.0 | 21.0 |
| Feldspar | 25.0 | 31.0 | 31.0 |
| Quartz | 19.0 | 17.0 | 22.0 |
| Soda ash | 3.5 | 3.5 | 3.5 |
| Sodium nitrate | 3.5 | 3.5 | 3.5 |
| Fluorspar | 5.0 | 5.0 | --- |
| Cryolite | 12.0 | 12.0 | 17.0 |
| Antimony oxide | 4.0 | 1.0 | 2.0 |
| Total | 100.0 | 100.0 | 100.0 |

Mill Batch:- Frit, 100.0; clay, 6.0; tin oxide, 7.0; magnesium carbonate, 0.5; water, 60.0

Table 4 - Glass Frits for Colored Enamels

Batch Compositions of Frits

| | A | B |
|---|---|---|
| Borax | 29.0 | 29.0 |
| Feldspar | 24.0 | 14.0 |
| Quartz | 30.0 | 38.0 |
| Soda ash | 10.0 | 10.0 |
| Sodium nitrate | 3.0 | 5.0 |
| Fluorspar | --- | 7.0 |
| Cryolite | 4.0 | 7.0 |
| Total | 100.0 | 100.0 |

Mill Batch:- Frit, 100.0; clay, 6.0; magnesium carbonate, 0.5; water, 50.0.

White enamels A, B, and C, given in Table 3, show a transition from those of the old German type to those now in use in American practice. There is a decrease in fluorspar with corresponding increase in cryolite, as well as a tendency to replace quartz by feldspar. The clay used as a mill addition may consist of some high grade ball clay or a plastic kaolin.

Glass frits for colored enamel, shown in Table 4, differ from frits for white enamels in that they are usually lower in opacifying agents and do not require the addition of tin oxide to the mill batch. Blue and black enamels are usually produced by adding metallic oxides to the batch previous to smelting, while other colors may be obtained by making suitable additions of stains or oxides in the milling. Examples of these are as follows:

Blue -- Glass A plus 4.0% black cobalt oxide and 2.0% manganese dioxide.

Black -- Glass A plus 1.5% cobalt oxide, 3.0% manganese dioxide, 1.0% chromium oxide, 0.5% copper oxide and 1.5% black iron oxide.

Other colors may be produced by additions of oxides or stains to Glass A or B in the mill:

Yellow -- 3 to 5% of cadmium sulphide

Green -- 3 to 5% of chromium oxide.

One to five per cent of stain with Glass A or B will produce other desired colors. These stains may be procured on the market, since they cannot be prepared successfully on a small scale in the individual plants.

Bureau of Standards
Oct. 11, 1930.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 166

# LABORATORY WEARING TEST TO DETERMINE THE RELATIVE WEAR RESISTANCE OF SOLE LEATHER AT DIFFERENT DEPTHS THROUGHOUT THE THICKNESS OF A HIDE

BY

REEVES W. HART, Assistant Physicist

*Bureau of Standards*

AUGUST 21, 1920

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1920

# LABORATORY WEARING TEST TO DETERMINE THE RELATIVE WEAR RESISTANCE OF SOLE LEATHER AT DIFFERENT DEPTHS THROUGHOUT THE THICKNESS OF A HIDE

By Reeves W. Hart

The results given in this report are those obtained from a series of preliminary tests and must not be regarded as the data from extensive researches on this subject. They are, however, significant in that for each individual test of this series the same general tendency is shown.

The leather used for these tests was taken from a single hide and so marked that the relative location of each test piece could be ascertained. The 18 test pieces prepared for the machine-wearing test were divided into 6 groups, 3 of which were tested by wearing with the grain side out, and 3 by subjecting the flesh side to the wearing action. The 6 groups were prepared as follows:

### TEST PIECES TO BE WORN ON THE GRAIN SIDE

$G_1$, left the original thickness of the leather.

$G_2$, made approximately two-thirds original thickness by skiving off one-third from the grain surface.

$G_3$, made approximately one-third original thickness by skiving off two-thirds from the grain surface.

### TEST PIECES TO BE WORN ON THE FLESH SIDE

$F_1$, left the original thickness of the leather.

$F_2$, made approximately two-thirds original thickness by skiving off one-third from the flesh side.

$F_3$, made approximately one-third original thickness by skiving off two-thirds from the flesh side.

By this procedure test pieces were obtained at four different layers of the leather, the grain surface, a depth of one-third the thickness of the leather, a depth of two-thirds the thickness, and the flesh surface.

Three individual tests were made on the wearing-test machine with a sample representing each group in every test. The length of the runs was varied, but all the other conditions of the tests were kept as nearly constant as possible.

The results of each of the three individual tests and also an average result of all of them are shown in the accompanying graphs. These graphs (Fig. 1) show the relative loss in weight of each sample as compared to the loss in weight of the sample G1, which was chosen as the basis for comparison. The arrangement of these graphs was based on the actual thickness of the test pieces. In each case there is a striking similarity between the results of the runs. From these data the outside surfaces of the leather appear to have much less resistance to wear than the interior portions of the hide. The grain surface has more resist-

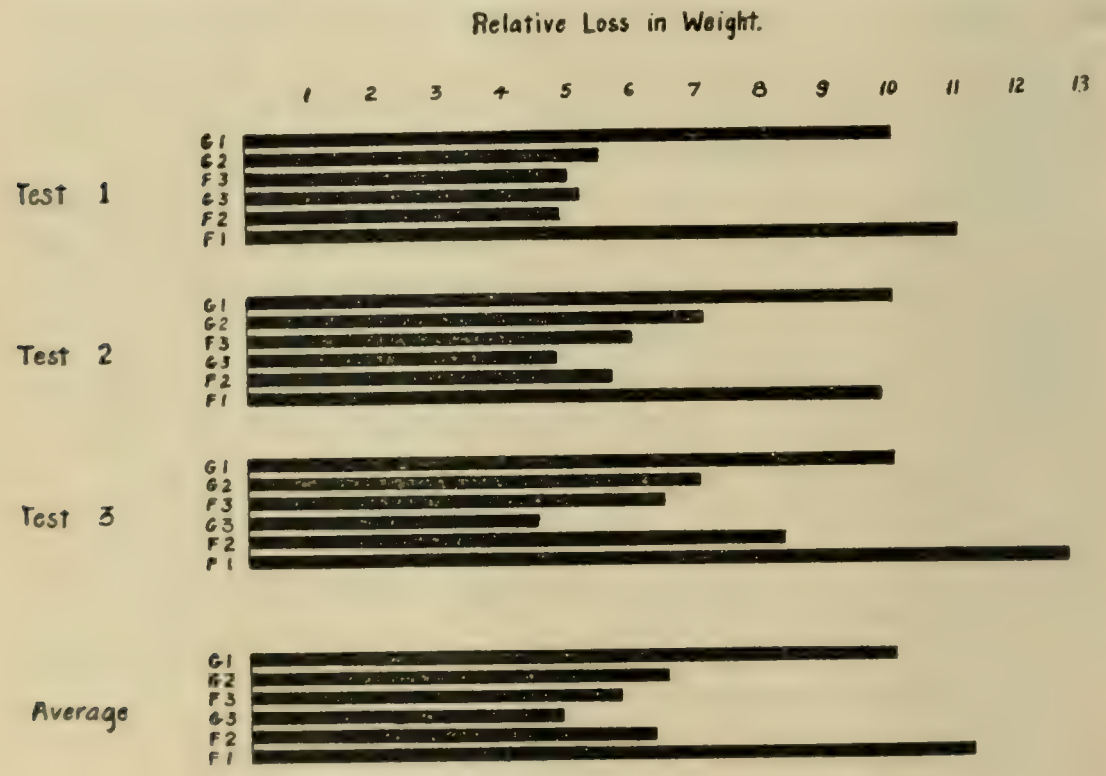


FIG. 1.—*Wear resistance at different depths of a hide*

ance than the flesh side, although this difference is not so marked as that between the outer and inner parts. Without extensive researches it would be impossible to locate the specific layer having the greatest wearing resistance, if any such surface exists, which is very doubtful.

There are several reasons to which this difference may be ascribed. It is probably due to a certain extent to the difference in the degree of tannage between the outer and the inner portions of the leather. The outer layers take up the tannin before the latter has a chance to penetrate to the interior of the hide; the tannins are precipitated in the surface layers and they, therefore, tend to retard the tanning of the central parts. In all pieces of

heavy leather the central part is probably much more lightly tanned than either the grain or the flesh surfaces. This may be clearly noticed in a piece of so-called undertanned sole leather.

A study of the anatomy of the hide itself discloses even greater reasons for this wide difference in wear resistance. The part of the skin that goes to make up the finished leather may be divided into two distinct parts, the grain and the flesh, or more correctly speaking, the corium. The chemical constitution and physical structure of these two divisions are quite different.

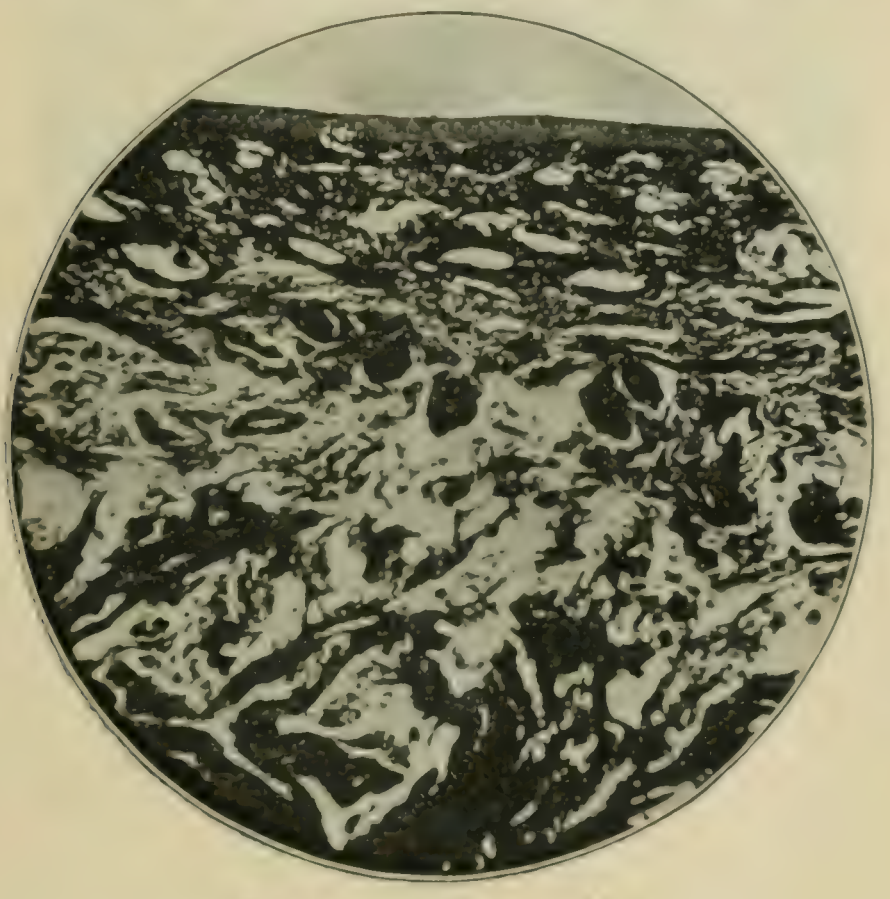

FIG. 2.—*Grain portion.* × 50

Briefly, the grain consists of the papillary layer, of bundles of very fine white and elastic fibers, and it contains the sudoriferous and sebaceous glands. These fine fibers are clearly defined, lying nearly flat and extending in every direction, closely interwoven and overlapping, sometimes even doubling back into the lower fibrous layers. Fig. 2 shows a cross section of the grain portion of a piece of lightly rolled union sole leather magnified to 50 diameters. The grain surface is seen as the dark portion at the top; beneath it may be seen the white fiber bundles with the glands scattered through them.

The corium, in Fig. 3, is composed of larger bundles or fine fibers, not so compactly interwoven as those of the grain portion.

There appears to be no system in which the fiber bundles interlace themselves, but, from his extensive researches on this subject, Alfred Seymour-Jones has concluded that these fiber bundles are woven in a definite steplike manner.[1]

The flesh side of the leather, Fig. 4, consists of smaller bundles of fibers closely interwoven and running more nearly parallel, forming a region similar to that formed by the white fibers of the grain.

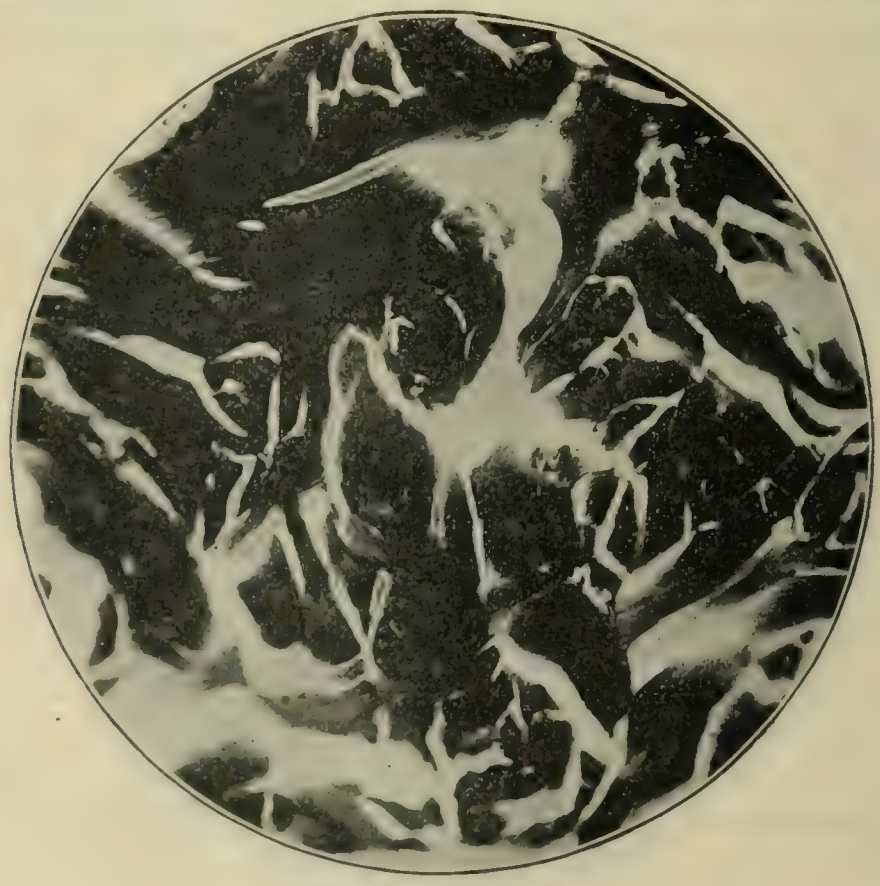

FIG. 3.—*Corium.* × 50

The grain membrane itself has very little resistance to wear. It deteriorates rapidly, especially in dyed leathers, and peels off in little flakes. Sheepskin and morocco (goat) leather show this defect, although it has been noted to a less extent in cow leather.[2] The surfaces composed of the smaller bundles of fiber, although more compactly woven, do not possess the resistance of the larger, less closely knitted fiber bundles of the corium.

[1] A. Seymour Jones, The physiology of the skin, Part XI.
[2] A. Seymour Jones, The physiology of the skin, Part VI.

From the data obtained from this series of tests the interior portions of the leather appear to have a greater resistance to wear

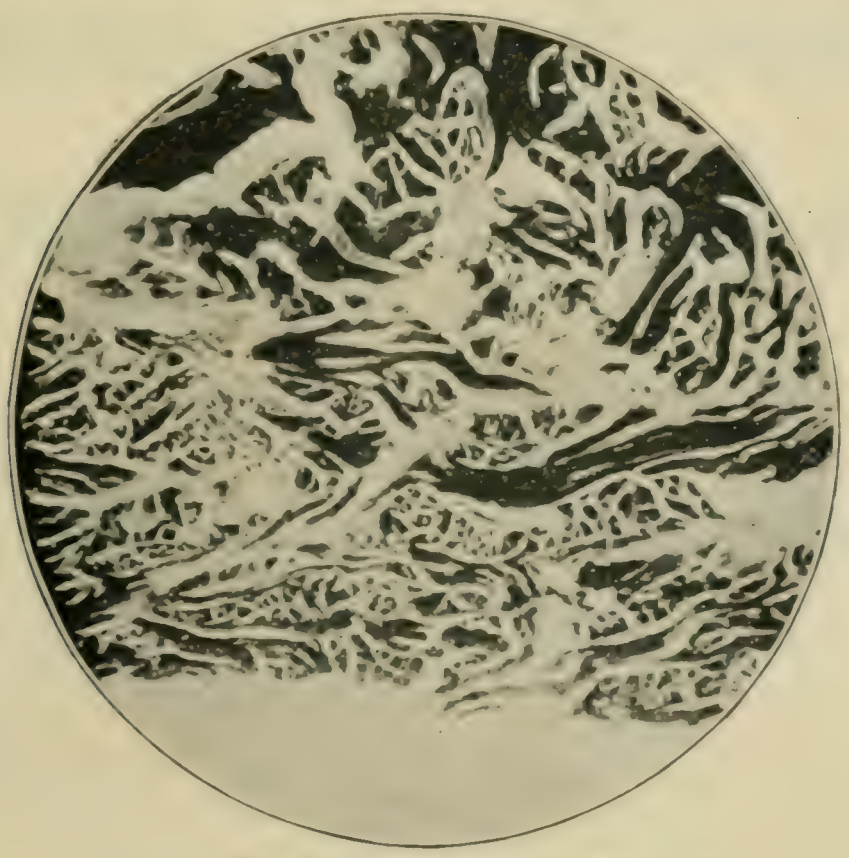

FIG. 4.—*Flesh portion.* × 50

than either the grain or the flesh sides. There is no specific surface which has the greatest wear resistance.

WASHINGTON, January 16, 1920.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 167

# AN EXAMINATION OF THE MUNSELL COLOR SYSTEM

## I. SPECTRAL AND TOTAL REFLECTION AND THE MUNSELL SCALE OF VALUE

BY

IRWIN G. PRIEST, Physicist
K. S. GIBSON, Associate Physicist
H. J. McNICHOLAS, Assistant Physicist
*Bureau of Standards*

SEPTEMBER 30, 1920

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1920

# AN EXAMINATION OF THE MUNSELL COLOR SYSTEM

## I. SPECTRAL AND TOTAL REFLECTION AND THE MUNSELL SCALE OF VALUE [1]

By Irwin G. Priest, K. S. Gibson, and H. J. McNicholas

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Elementary theory involved in this report | 5 |
| III. Experimental data | 7 |
| IV. Discussion of Munsell value scale | 20 |
| V. Proposals for the improvement of the system and its establishment upon a more reliable foundation | 32 |


## I. INTRODUCTION

A signal and practical contribution to the classification and specification of colors for the purposes of art was made by A. H. Munsell in his book, A Color Notation,[2] and The Atlas of the Munsell Color System.[3] The limits of this paper will not permit of a detailed review of these books, and readers unfamiliar with the subject are referred to the citations just given. It must suffice here to point out that Munsell has adopted the only natural and logical method of color classification, as has, indeed, been expounded by Bezold, Rood, Abney, Nutting,[4] and others. In this natural method a color is specified completely by three characteristics which have been designated by various terms, the meanings of which, as used by different authorities, are shown in Table 1.

[1] This paper is an amplification of report on Bureau of Standards Test No. 23998 to Munsell Color Co., June, 1917.

[2] A. H. Munsell, A Color Notation, Boston, Geo. H. Ellis Co.; 1905. Later editions, 1907, 1913, 1916.

[3] Boston, Wadsworth, Howland & Co., 1915.

[4] Bezold, Theory of Color, English Translation by Koehler, Am. Ed., p. 102; 1876. Rood, Modern Chromatics, New York, 1879. Abney, Color Measurement and Mixture, London, 1891. Nutting, B. S. Bulletin, 9, p. 1, 1913. For the concept of colors arranged in a sphere, consult particularly: (1) Philip Otto Runge, Die Farbenkugel, Hamburg, 1810. (Reprinted in Runge's Hinterlassene Schriften, p. 113; Hamburg, 1840. Copy in Boston Public Library.) (2) Parsons, Introduction to Study of Color Vision, p. 58. (3) Külpe, Outlines of Psychology, 1895. English translation by Titchener, p. 112, 1901. Cf. also: (4) Chevreul, Exposé d'un moyen de définir et de nommer les couleurs . . . , Mem. de l'Academie, Paris, **33**, 1861. (5) Hofler, Zeit. fur Physiol. und Psyc. der Sinnesorg. Abt. 1, **58**, pp. 356–371; 1910–1911.

**TABLE 1.—The Three Characteristics of Color, and the Names by which These Characteristics are Designated by Various Authorities**

| Authority | The species of color. The characteristic by virtue of which it may be referred with more or less accuracy to the spectral colors, red, orange, yellow, green, blue, violet | The characteristic in which colors vary from gray (a color having no hue) to colors having a pronounced hue | The characteristic by which grays may be arranged in series between white and black |
|---|---|---|---|
| Bezold [a] | Hue | Purity | Brightness. |
| Rood [b] | Hue | Purity | Luminosity or brightness. |
| Abney [c] | Hue | Purity | Luminosity. |
| Century Dictionary [d] | Color tone or hue | Chroma or saturation | Brightness, luminosity, value, or tone. |
| Webster's Dictionary [e] | Hue or color tone | Chroma, purity, intensity, or saturation. | Value or luminosity. |
| Standard Dictionary [f] | Color tone or quality | Purity or saturation | Brightness. |
| MUNSELL | HUE | CHROMA | VALUE. |

[a] The Theory of Color, English translation by Koehler, American Ed., p. 100; 1876.
[b] Modern Chromatics, p. 30 ff.; 1879.
[c] Color Measurement and Mixture, p. 15; 1891.
[d] Century Dictionary (1902 and Revised Ed., 1911) under "Color," "Value," and "Tone."
[e] Webster's International Dictionary (1910) under "Color."
[f] Standard Dictionary (1916) under "Color."

Munsell has expounded this system in an elementary and practical way for students of art and has accomplished the colossal task of producing an altas of charts in which actual colored samples are shown arranged according to this natural system. That the system is valuable in practice is demonstrated by the fact that it has been used for several years with great satisfaction and success in connection with the business of one of the foremost manufacturers of colored printing inks.[5] From the point of view of precise colorimetry, however, the system, as it exists to-day, is faulty because of its lack of fundamental accurate specification. Much of the knowledge and methods of measurement that are available now were not available to Mr. Munsell, whose death has prevented the improvements and revision which it is to be presumed he would have made had he lived. After Mr. Munsell's death the Munsell Color Co.[6] requested the Bureau of Standards to undertake this fundamental standardization,[7] and submitted for this purpose the set of cards herein considered. We have no extensive information as to the uniformity of various sets which the company may have issued.

This paper is a partial report upon this task. It deals only with (1) the diffuse spectral reflection of the nine neutral grays and three samples of each of the hues red, yellow, green, blue, and

[5] By Arthur S. Allen, with a corporation having headquarters in New York City.
[6] Then at 220 West Forty-second Street, New York City, since removed to 120 Tremont Street, Boston, Mass.
[7] Letters of July 19 and Aug. 8, 1918, Munsell Color Co. to Bureau of Standards.

purple; (2) a discussion of the Munsell value scale; (3) recommendations on the improvement of the system and its establishment upon a more secure foundation. A complete report would comprehend experimental determinations of the hue, value, and chroma of all the standards, a task which it has not been possible to undertake as yet. The results here reported are considered of prime importance (*a*) as regards the basis of the system and (*b*) as being logically the first part of the standardization.

## II. ELEMENTARY THEORY INVOLVED IN THIS REPORT

Light is radiant power which, impinging on the retina of the eye, excites the sensation called color.[8] The radiant energy may be considered as traveling through the space between the light source and the retina in the form of a vibration or wave motion in a hypothetical intervening medium. If the vibration has some one definite frequency, the color produced will have a pronounced hue, which may be described as red, orange, yellow, green, blue, or violet, depending upon that frequency. (See Table 2.) The

TABLE 2.—Approximate Frequencies and Wave Lengths[a] of Spectral Hues

| Hue | Frequency in vibrations per trillionth of one second | Wave length[b] in millimicrons |
|---|---|---|
| Red | 429 | 700 |
| Orange | 502 | 597 |
| Yellow | 516 | 581 |
| Green | 570 | 527 |
| Blue | 634 | 473 |
| Violet | 739 | 406 |

[a] Cf. Rood, Modern Chromatics, p. 26, 1879.

[b] One millimicron $= \frac{\text{micron}}{1\,000} = \frac{1}{1\,000\,000}$ millimeter $=$ about $\frac{1}{25\,400\,000}$ inch.

color will also be very saturated; that is, of high chroma. If the energy is distributed according to a law not yet determined with precision, but (in one case) approximately represented in sunlight, among many vibrations of different frequencies, the color will be recognized as white (or gray) and will have no distinguishing hue. If the energy is distributed among vibrations of different frequencies according to some law other than that required to produce white or gray, it may produce any of a vast number of colors of various hues and chromas, depending upon the relative amounts

[8] Rigorously, light is radiant power multiplied by a factor proportional to its visibility. This factor varies with the frequency or wave length of the energy. Power is the time rate of transfer of energy.

of energy of different frequencies. In Fig. 1 are shown typical examples of the distribution of energy among various wave lengths required to produce various colors. The horizontal scale is a scale of wave lengths. The vertical scale is a scale of relative energy. Note, in the figure, that red is produced by a preponderance of energy of wave lengths about 600 to 700 mμ;[9] green, 500 to 600 mμ; blue, 400 to 500 mμ. These curves are intended merely to illustrate a few typical cases of spectral-energy distributions which produce certain colors. It will be understood readily that the possible variety of such curves is infinite. To each curve there corresponds a color of a certain hue and chroma, and such a curve

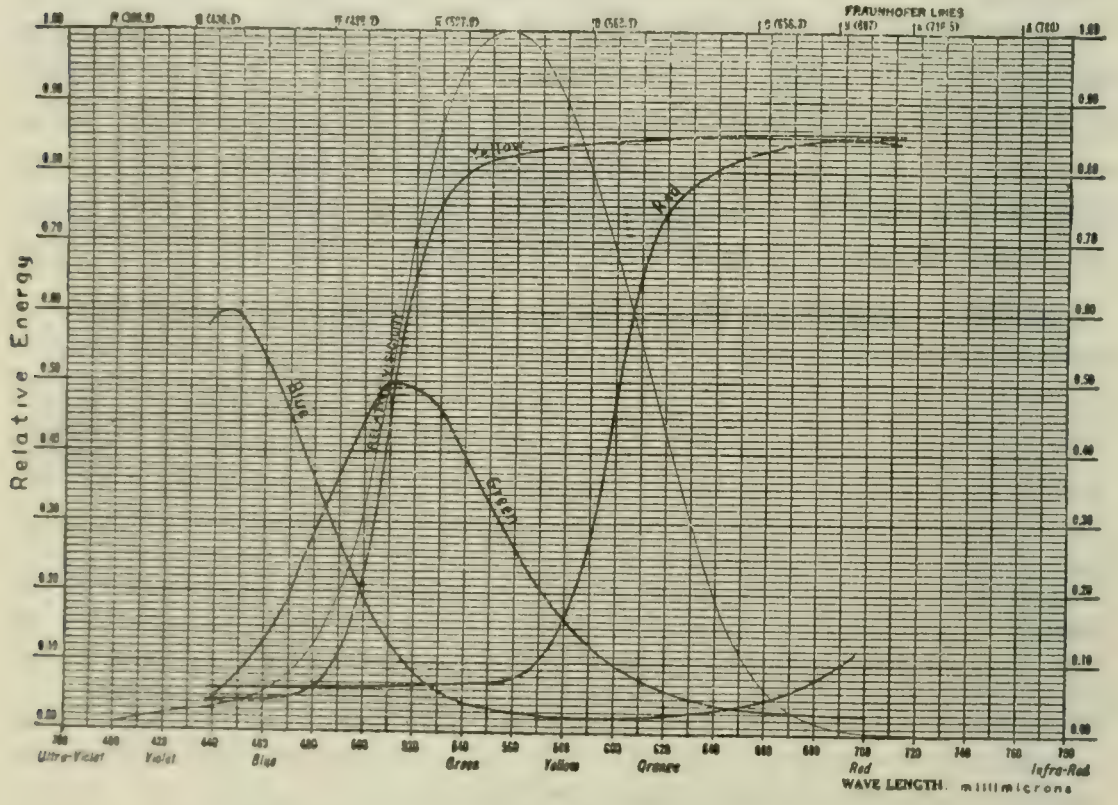



FIG. 1

is therefore sufficient to determine uniquely hue and chroma, although the process of deriving these characteristics from such curves is very laborious and has not yet been sufficiently standardized [10] for practical use. Nevertheless, such a curve of spectral-energy distribution, together with total luminosity or value, completely specifies a color by specifying its stimulus. (The converse is not true; that is, a given color may be excited by energy represented by any of a considerable number of distribution curves. The number of possible colors is therefore not infinite.)

[9] mμ = one millimicron = 0.001 micron = one millionth of one millimeter = about $\frac{1}{25\,400\,000}$ inch.

[10] Methods have been indicated by H. E. Ives, Jour. Frank. Inst., p. 673; Dec., 1915.

Keeping in mind the conception of a spectral-energy distribution curve as discussed above, let us now consider the color of a diffusely reflecting surface such as one of the cards in the Munsell Atlas.[11] Let this card be illuminated by diffuse white light. If it reflects light of all frequencies equally well, it will appear gray, or, in the extreme cases, white or black, the luminosity and the Munsell value being determined by the total light reflected. (See Fig. 2.) If, on the other hand, the card is selective in its reflection—that is, reflects light of some frequencies or wave lengths much better than others—its color will, in general, be distinguished by some hue. The saturation or chroma of the color will be roughly indicated by the shape of the spectral-reflection curve; if its reflection is small or zero for a large range of wave lengths and large for another small range, the color will be very saturated—that is, of high chroma—while only a slight variation in the reflection for different wave lengths will indicate a pale color; that is, one slightly saturated or of low chroma.

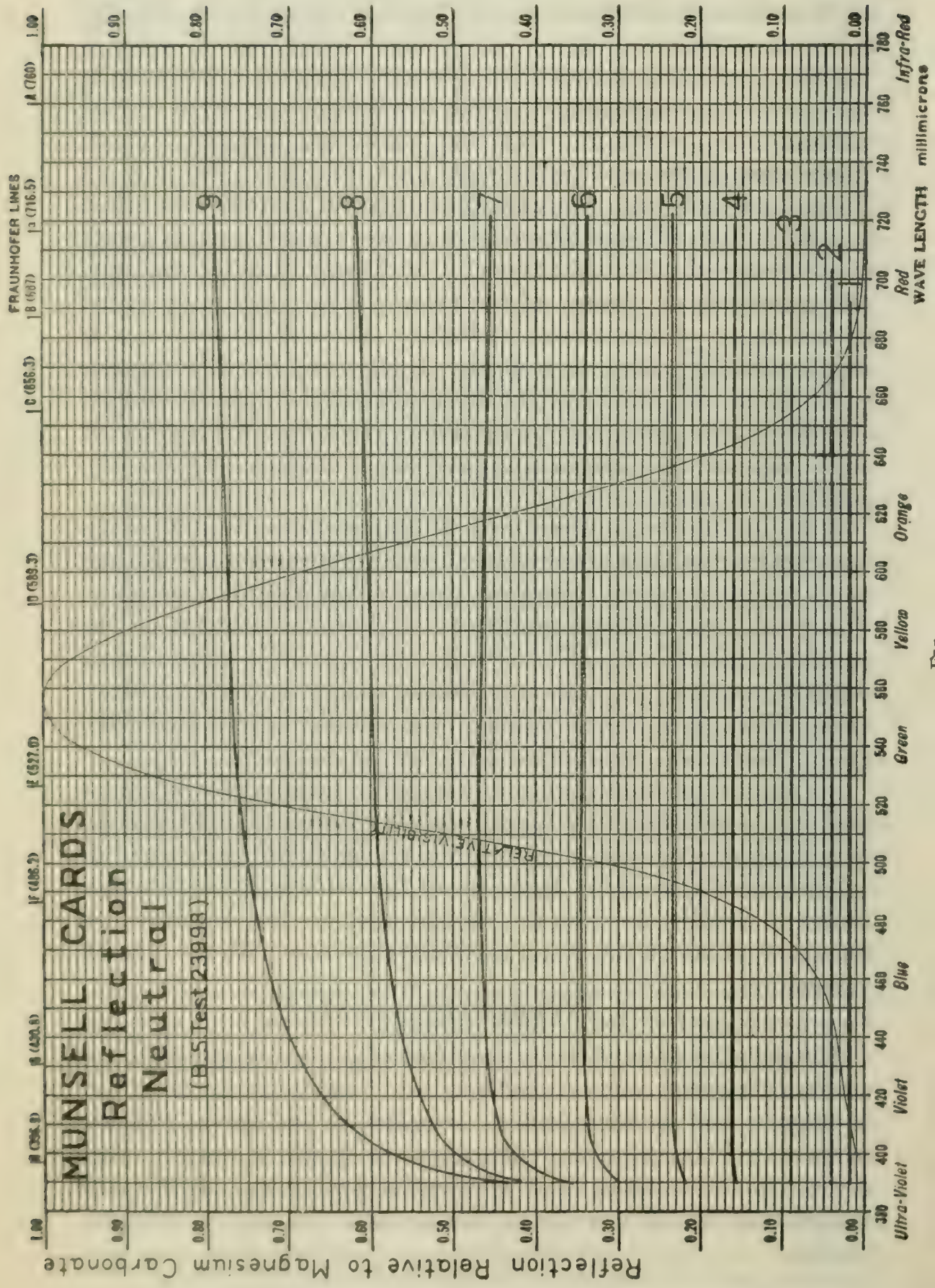
It is possible to measure, with a spectrophotometer, for each wave length, the light reflected by the card relative to that reflected by a standard white substance such as magnesium carbonate. This ratio is the *reflection* relative to magnesium carbonate. The absolute reflection equals this ratio multiplied by the absolute reflection (that is, the ratio of reflected to incident light) of magnesium carbonate. (The value of the absolute reflection of magnesium carbonate is not very certainly established.)

For the reason that the least perceptible increment in stimulus is directly proportional to the stimulus, it is better to plot reflection to a logarithmic scale, as is done in Figs. 2*a* to 7*a*, inclusive. As will be pointed out in the discussion of the value scale below, value should naturally be directly proportional to the logarithm of reflection, although this is not accurately the case with the Munsell values.

## III. EXPERIMENTAL DATA

The primary data of the present investigation are shown in the curves of spectral reflection in Figs. 2 to 7 and 2*a* to 7*a*, inclusive. In Figs. 2 and 2*a* the numbers attached to the curves indicate value on the Munsell scale. The fractions $^{7}/_{1}$, $^{6}/_{1}$, $^{8}/_{2}$, etc., in other figures, indicate value and chroma according to the Munsell designations, the numerator indicating value and the denominator chroma.

[11] A *perfect* diffusely reflecting surface would appear equally bright from all directions [illegible]


MUNSELL CARDS
Reflection
Neutral
(B.S.Test 23998)
Reflection Relative to Magnesium Carbonate
RELATIVE VALUE
FRAUNHOFER LINES
WAVE LENGTH millimicrons
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
300
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
720
740
760
780
1
2
3
4
5
6
7
8
9

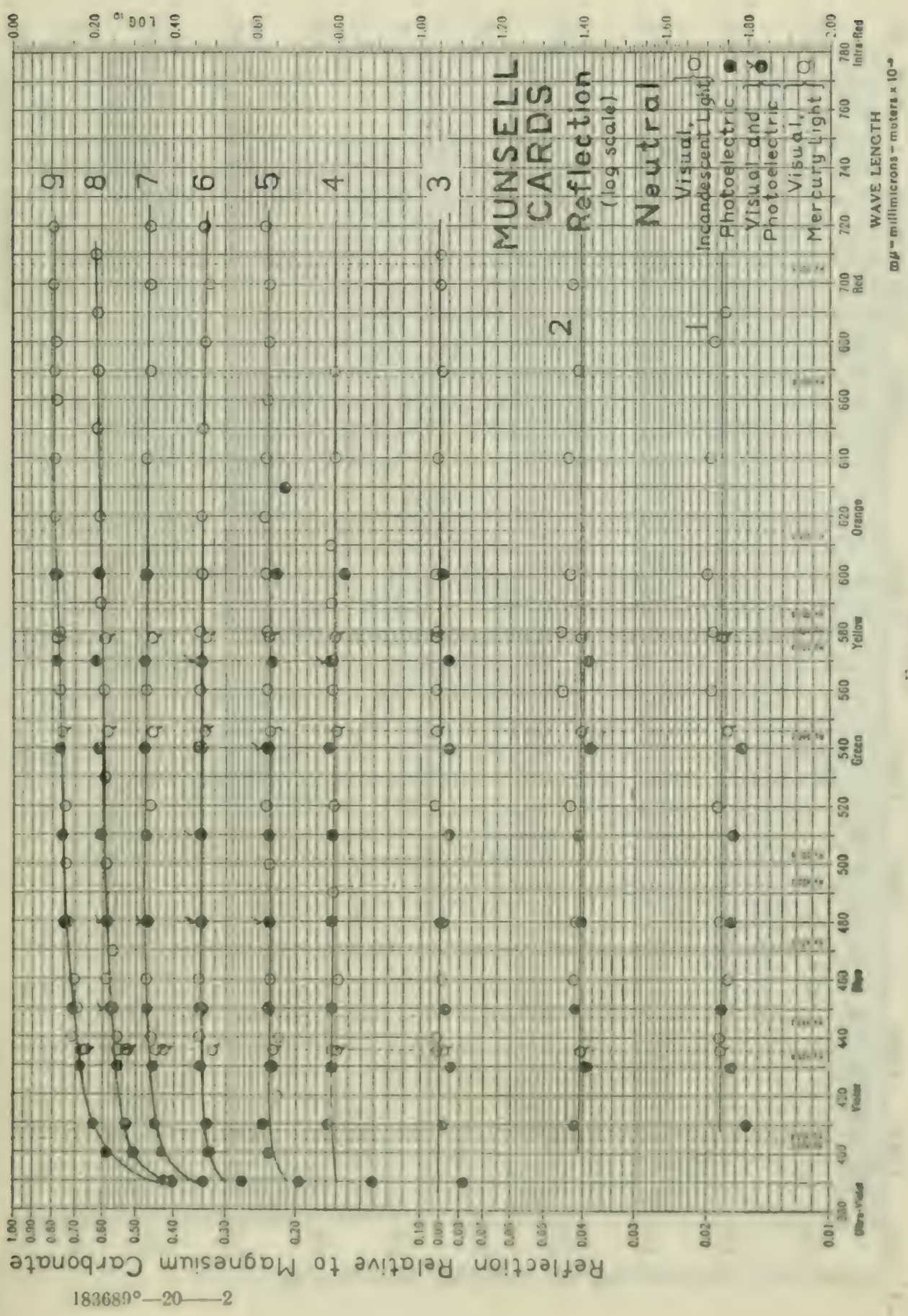
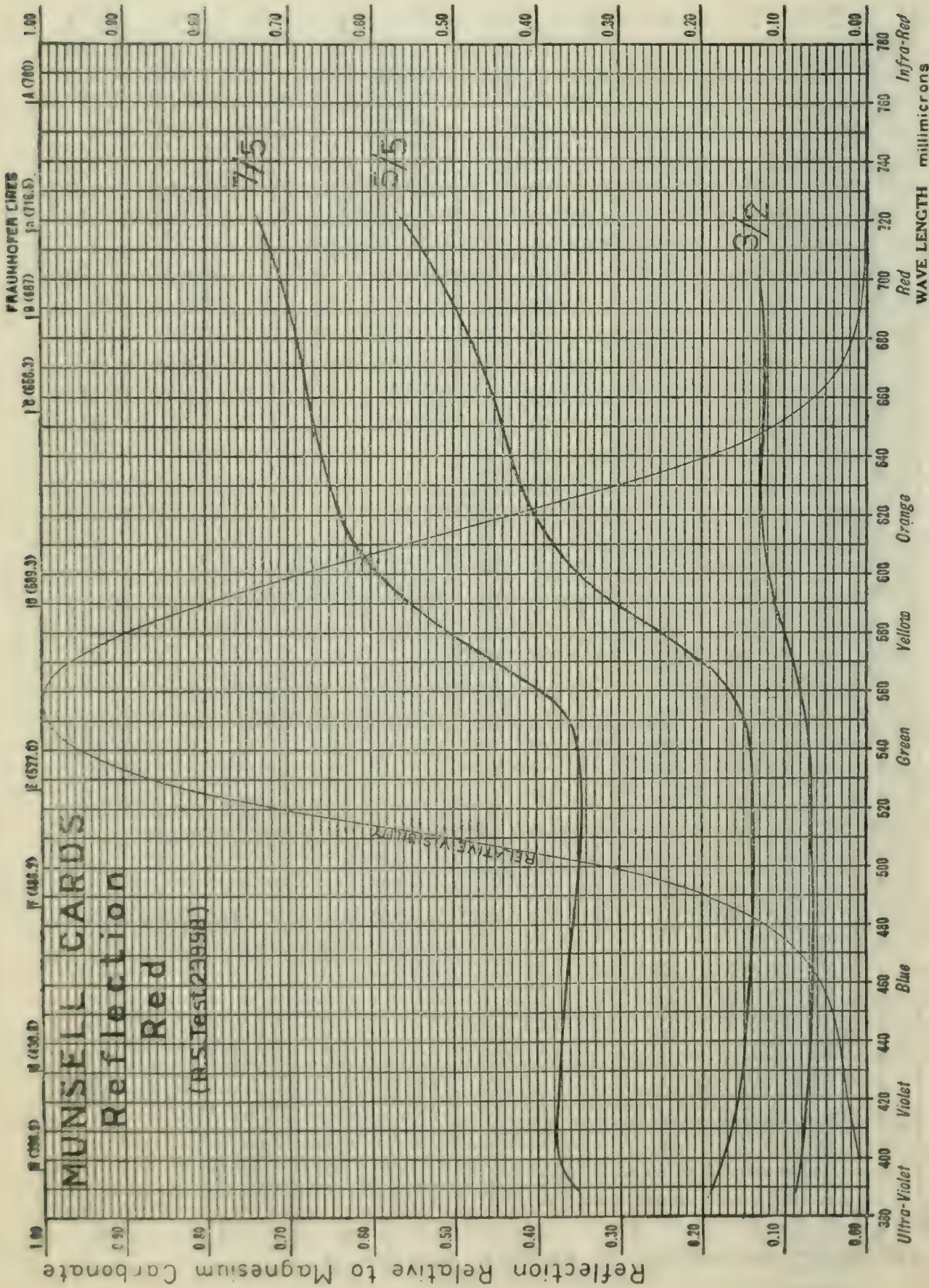

MUNSELL CARDS
Reflection (log scale)
Neutral
Visual, Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
WAVE LENGTH
mμ = millimicrons = meters × 10⁻⁹
Reflection Relative to Magnesium Carbonate
9
8
7
6
5
4
3
2
1

FIG. 2a


MUNSELL CARDS
Reflection
Red
(N.B.S. Test 23398)
RELATIVE VISIBILITY
FRAUNHOFER LINES
Reflection Relative to Magnesium Carbonate
WAVE LENGTH millimicrons
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
5/5
5/8
5/2

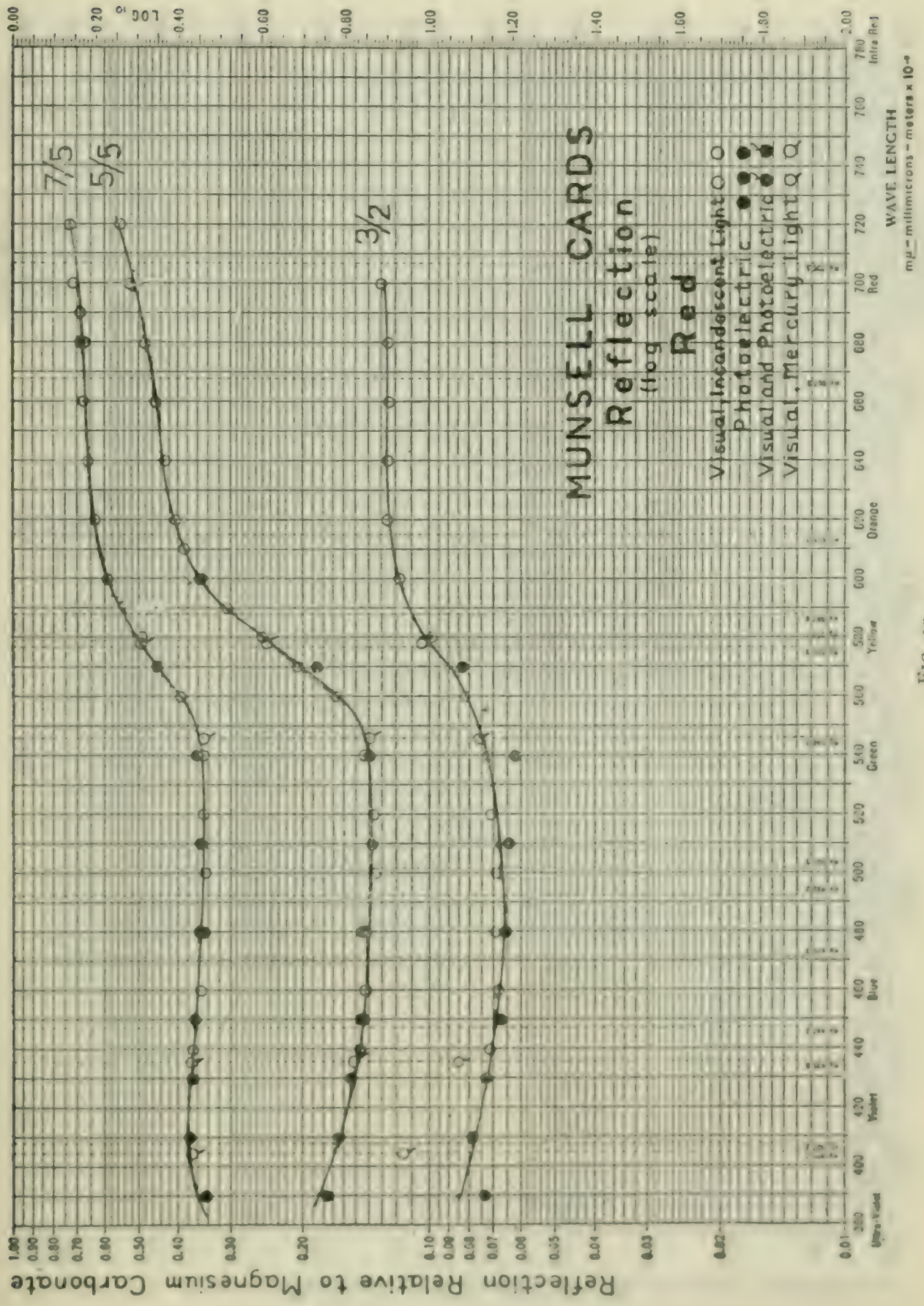
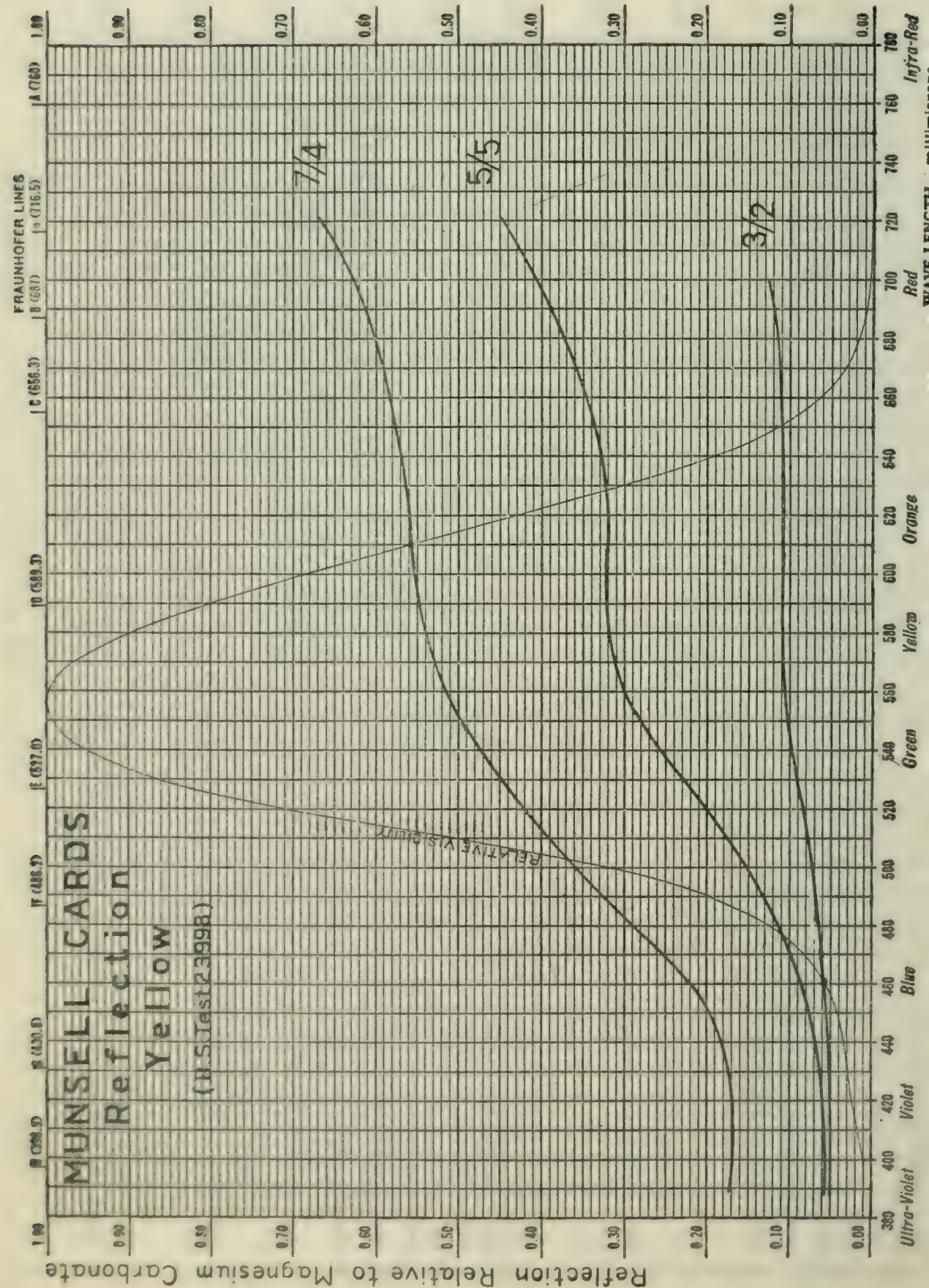

MUNSELL CARDS
Reflection
(log scale)
Red
Visual Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
7/5
5/5
3/2
Reflection Relative to Magnesium Carbonate
WAVE LENGTH
mμ = millimicrons = meters x 10⁻⁹

FIG. 34


MUNSELL CARDS
Reflection
Yellow
(N.B.S. Test 23998)
7/4
5/5
3/2
RELATIVE VISIBILITY
FRAUNHOFER LINES
Reflection Relative to Magnesium Carbonate
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
WAVE LENGTH

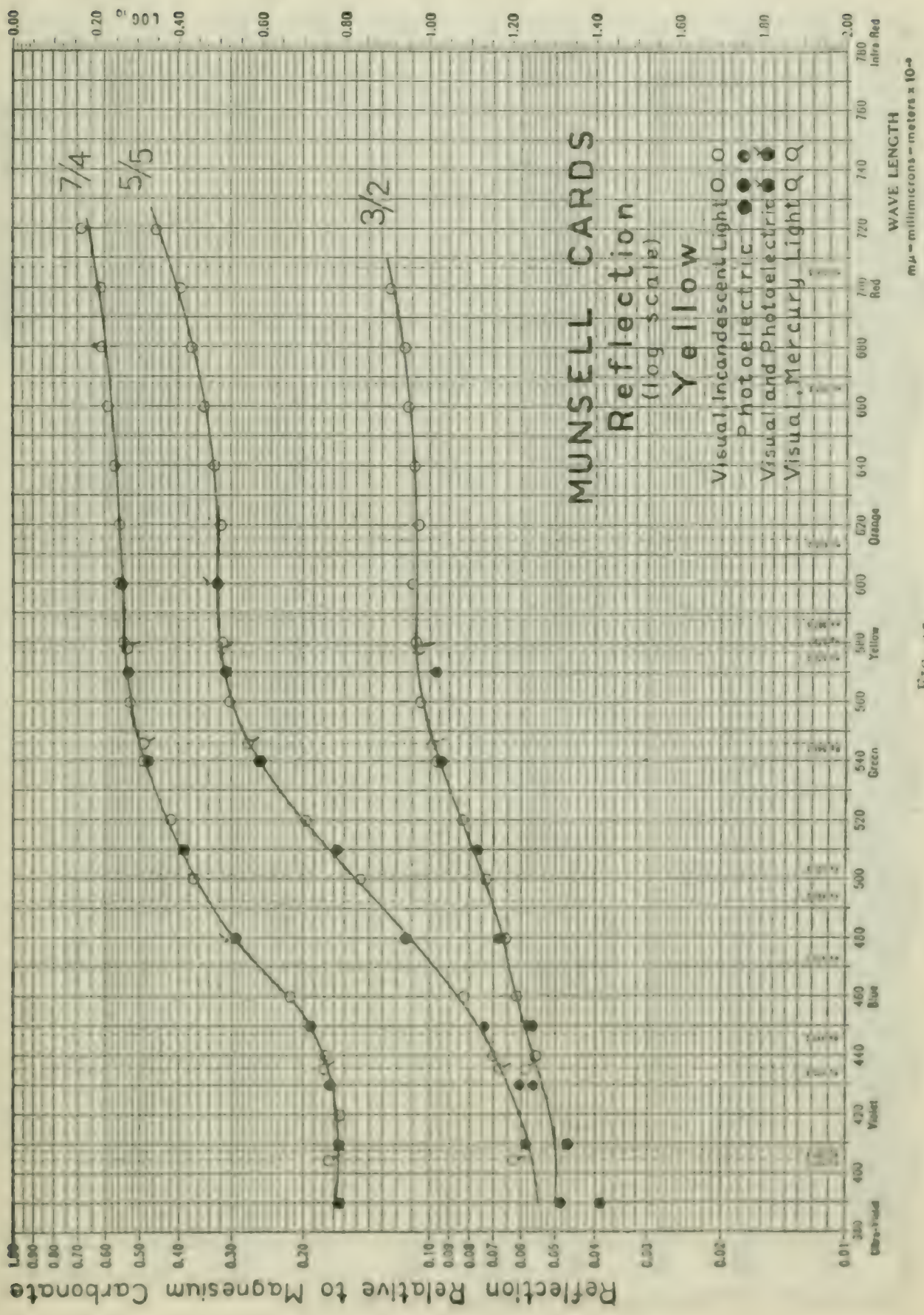
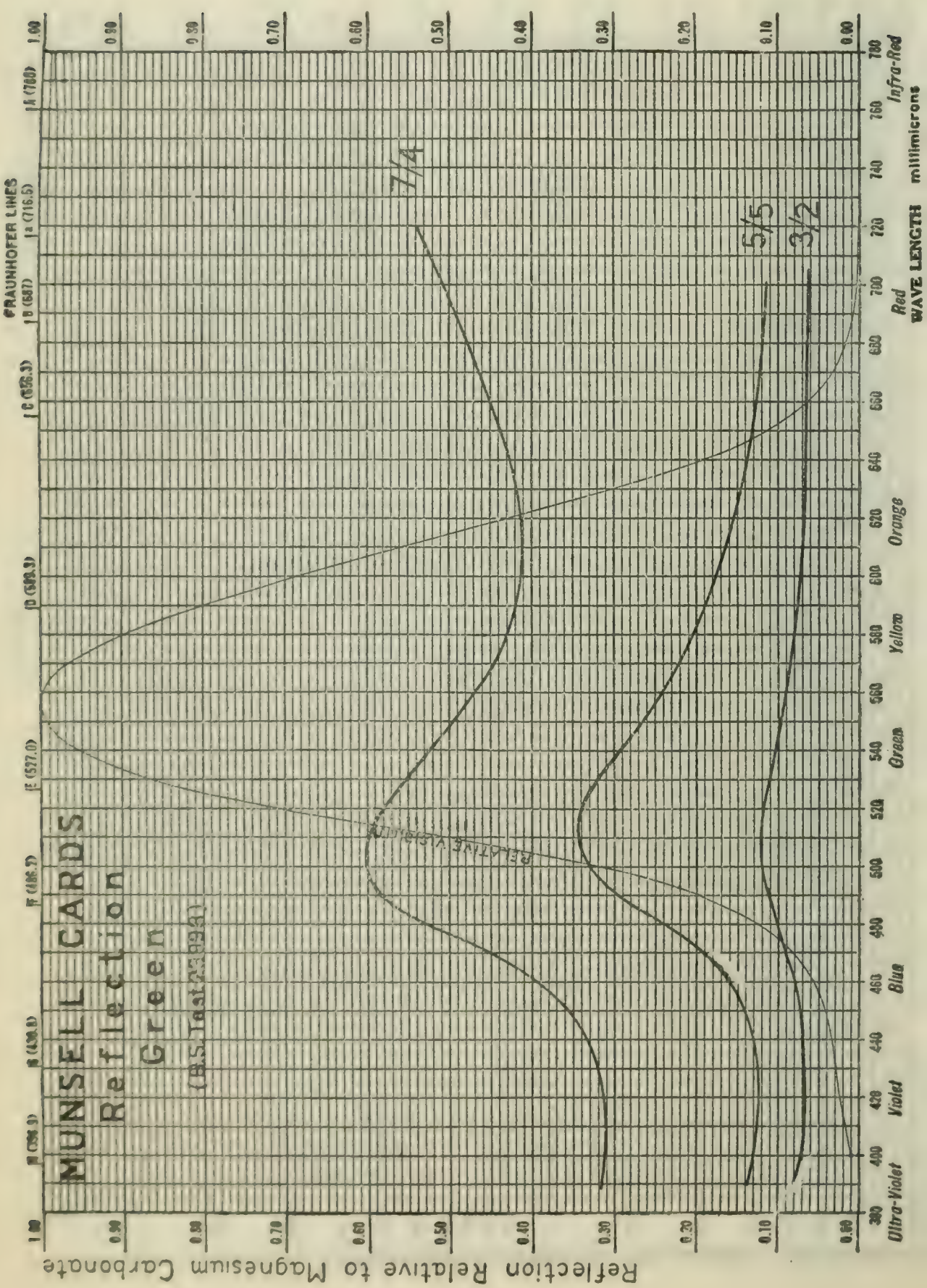

MUNSELL CARDS
Reflection
(log scale)
Yellow
Visual, Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
7/4
5/5
3/2
WAVE LENGTH
mμ - millimicrons - meters x 10-9
Reflection Relative to Magnesium Carbonate

FIG. 4a


MUNSELL CARDS
Reflection
Green
(B.S. Test 23993)
Reflection Relative to Magnesium Carbonate
WAVE LENGTH millimicrons
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
FRAUNHOFER LINES
7/4
5/5
3/2

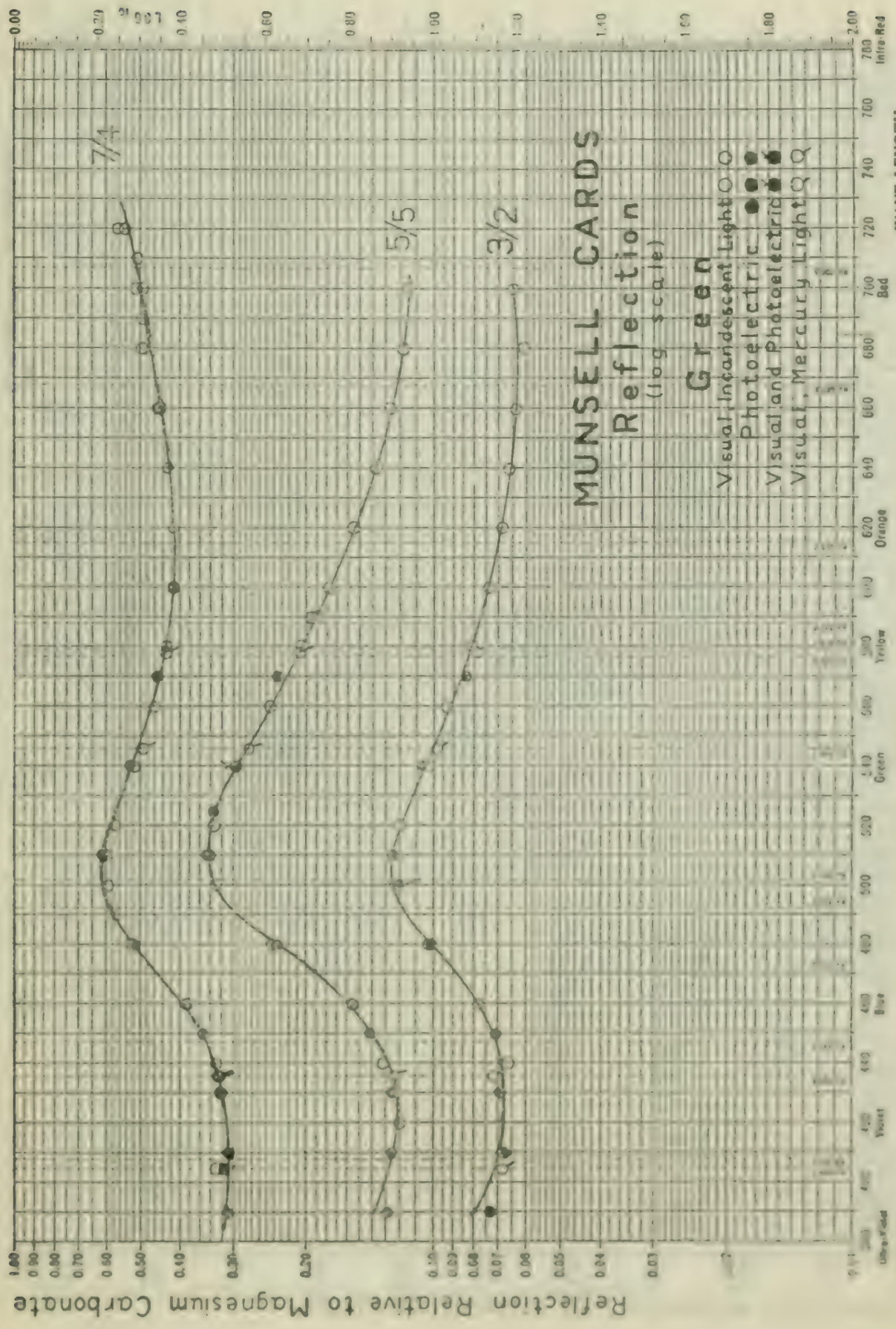

MUNSELL CARDS
Reflection
(log scale)
Green
Visual, Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
7/4
5/5
3/2
WAVE LENGTH
mμ = millimicrons = meters x 10⁻⁹
Reflection Relative to Magnesium Carbonate

FIG. 5a

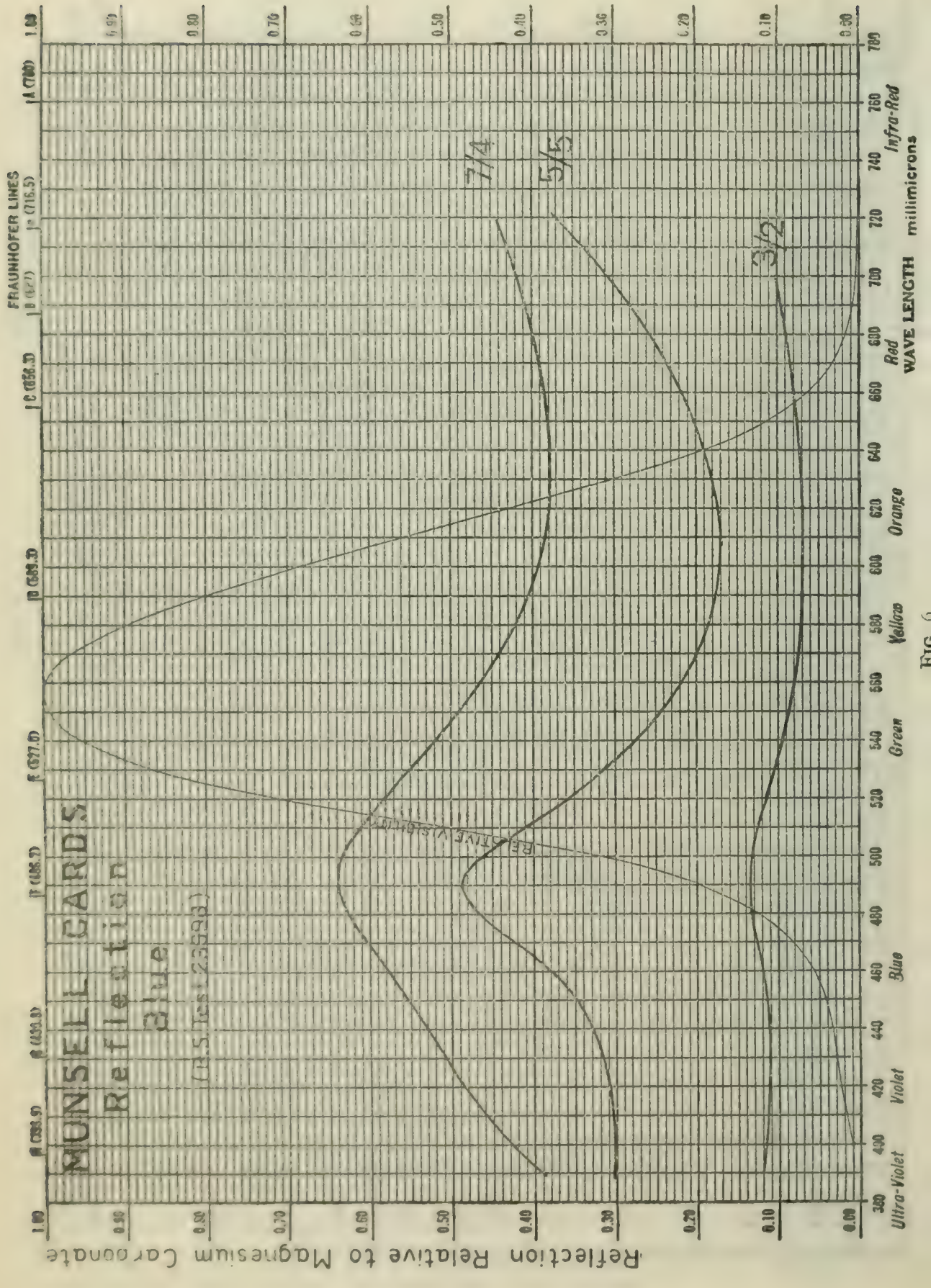

MUNSELL CARDS
Reflection
Blue
(B.S. Test 23598)
Reflection Relative to Magnesium Carbonate
RELATIVE VISIBILITY
FRAUNHOFER LINES
WAVE LENGTH millimicrons
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
3/4
5/5
3/2

FIG. 6

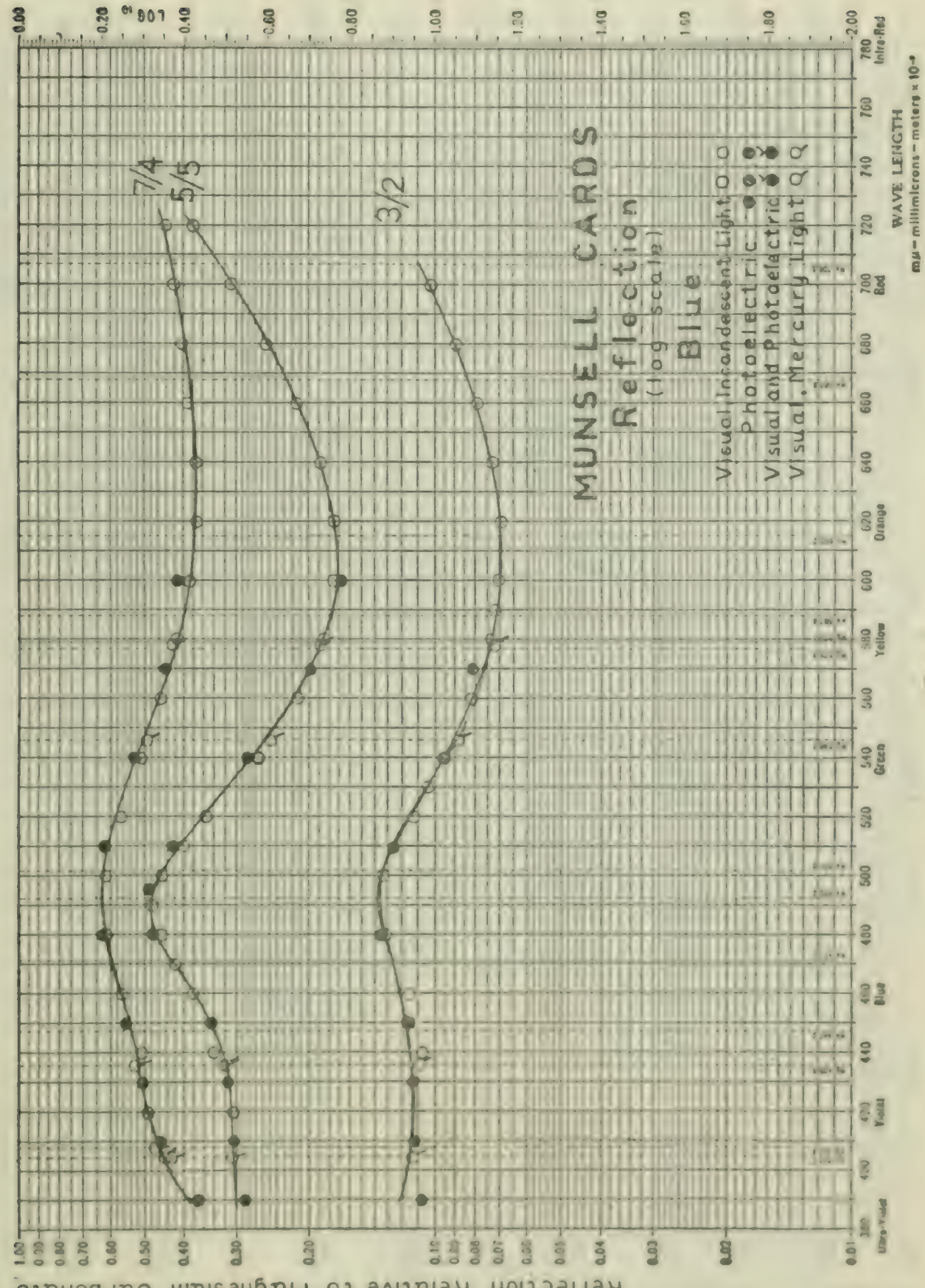

MUNSELL CARDS
Reflection
(log scale)
Blue
Visual, Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
7/4
5/5
3/2
WAVE LENGTH
mμ – millimicrons – meters × 10⁻⁹
Reflection Relative to Magnesium Carbonate

FIG. 6a

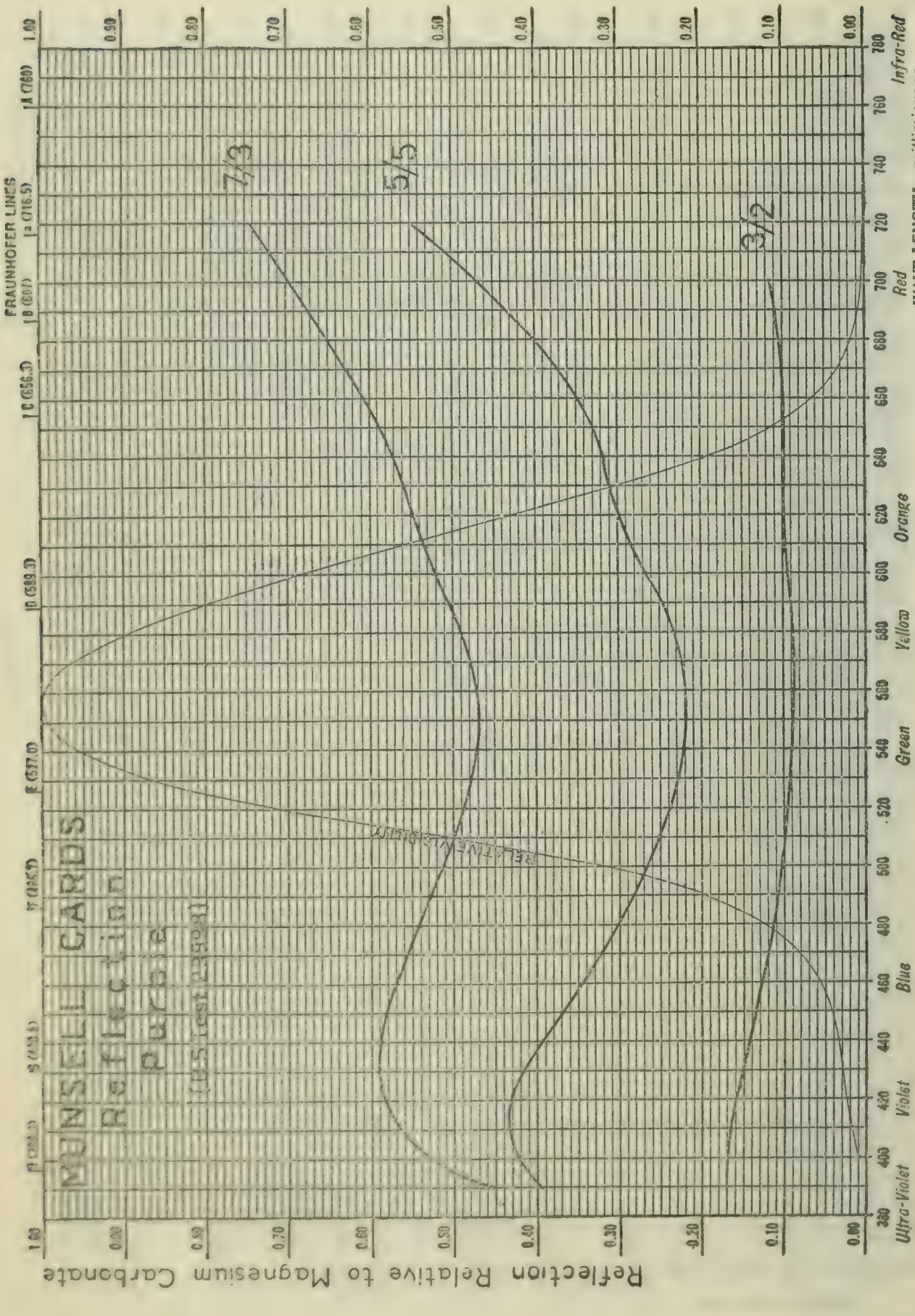

MUNSELL CARDS
Reflection
(Bruce Preble)
7/3
5/5
3/2
RELATIVE VISIBILITY
Reflection Relative to Magnesium Carbonate
WAVE LENGTH millimicrons
Ultra-Violet
Violet
Blue
Green
Yellow
Orange
Red
Infra-Red
FRAUNHOFER LINES

FIG. 7

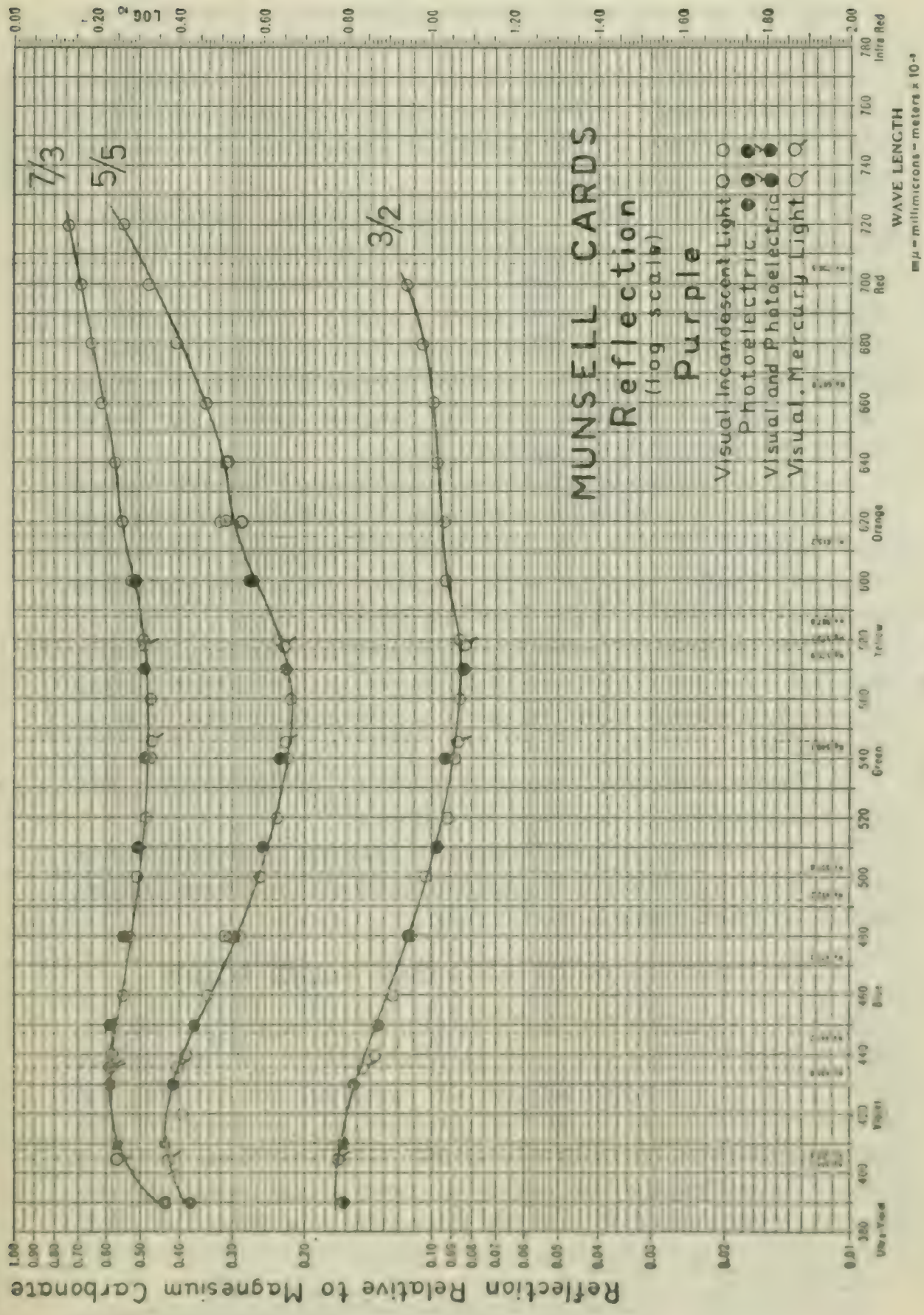

MUNSELL CARDS
Reflection
(Hog scale)
Purple
Visual Incandescent Light
Photoelectric
Visual and Photoelectric
Visual, Mercury Light
7/3
5/5
3/2
WAVE LENGTH
μ = millimicrons = meters x 10⁻⁹
Reflection Relative to Magnesium Carbonate

Fig. 7a

It is not necessary for the purpose of this report to describe in detail the methods used in obtaining these data. For those who are interested in the methods the following information is given:

(1) The visual data were obtained by the Koenig-Martens spectrophotometer,[12] with an illumination apparatus designed for such measurements at the Bureau of Standards. The essential features of this apparatus are:

(*a*) The sample and the standard magnesium carbonate are illuminated by lamps in a white-lined box in such a way that the illumination is, so far as these samples are concerned, equivalent to perfectly diffuse; that is, of equal intensity from all directions. Either the light from gas-filled tungsten lamps or mercury-vapor lamps may be used at will. In the graphs herewith, the plain open circles indicate data with the tungsten lamps, the circles with a tail, data with the mercury lamps.

(*b*) The spectrophotometer looks into this box through a small aperture and in a direction normal to the surfaces of the sample and standard, so that one-half of the photometric field is illuminated by light reflected by the standard magnesium carbonate and the other half by light from the Munsell card.

(*c*) The magnesium-carbonate block and the card can be interchanged conveniently by a rotating device, and relative reflection is computed by the standard *tan* × *cot* formula for this spectrophotometer.

(2) The photoelectric data were obtained by the method and apparatus previously described by Gibson.[13]

The very close agreement throughout between the data obtained by these entirely different methods is convincing evidence that no serious errors of methods are involved.

## IV. DISCUSSION OF MUNSELL VALUE SCALE

In Fig. 8 is shown the approximate average spectral distribution of light from the noon sun at Washington.[14] If, for each of a series of wave lengths through the spectrum, we multiply the ordinates of this curve by the corresponding ordinates of the spectral reflection curve of any sample, and plot these products against wave lengths, we obtain a curve which represents the spectral distribution of sunlight after reflection from the card.

[12] Ann der Phys. (4), 12, p. 984; 1903.

[13] Jour. Op. Soc. of Am., p. 23; Jan.–Mar., 1919. B. S. Sci. Paper No. 349; Oct., 1919.

[14] Representative curve based on visibility data by Coblentz and Emerson (B. S. Scientific Paper No. 301) and energy distribution adopted by Priest (Phys. Rev. (2), 11, p. 504, Fig. 1) from the data of Abbot.

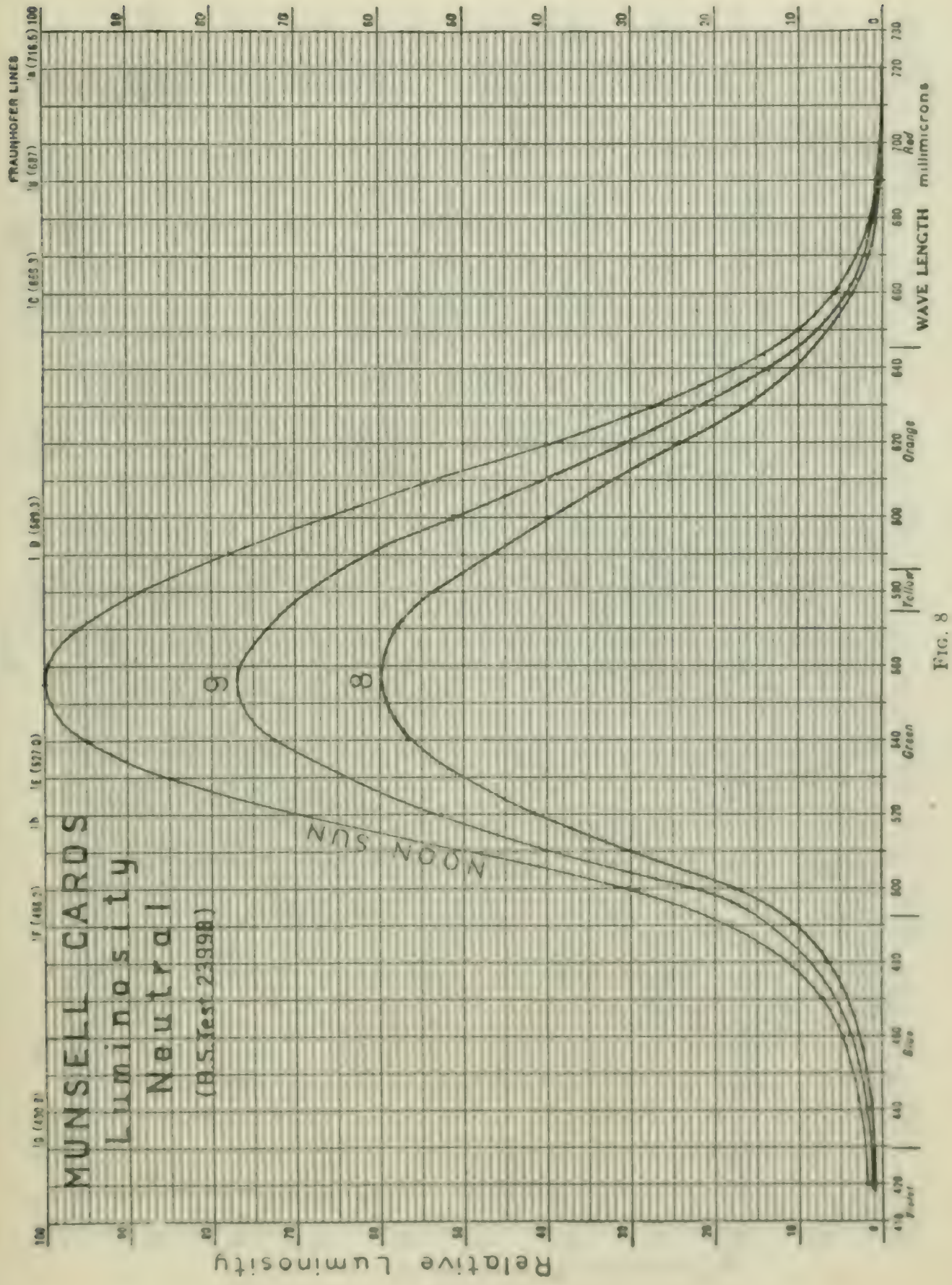

MUNSELL CARDS
Luminosity
Neutral
(B.S. Test 23998)
NOON SUN
9
8
Relative Luminosity
WAVE LENGTH millimicrons
FRAUNHOFER LINES

FIG. 8

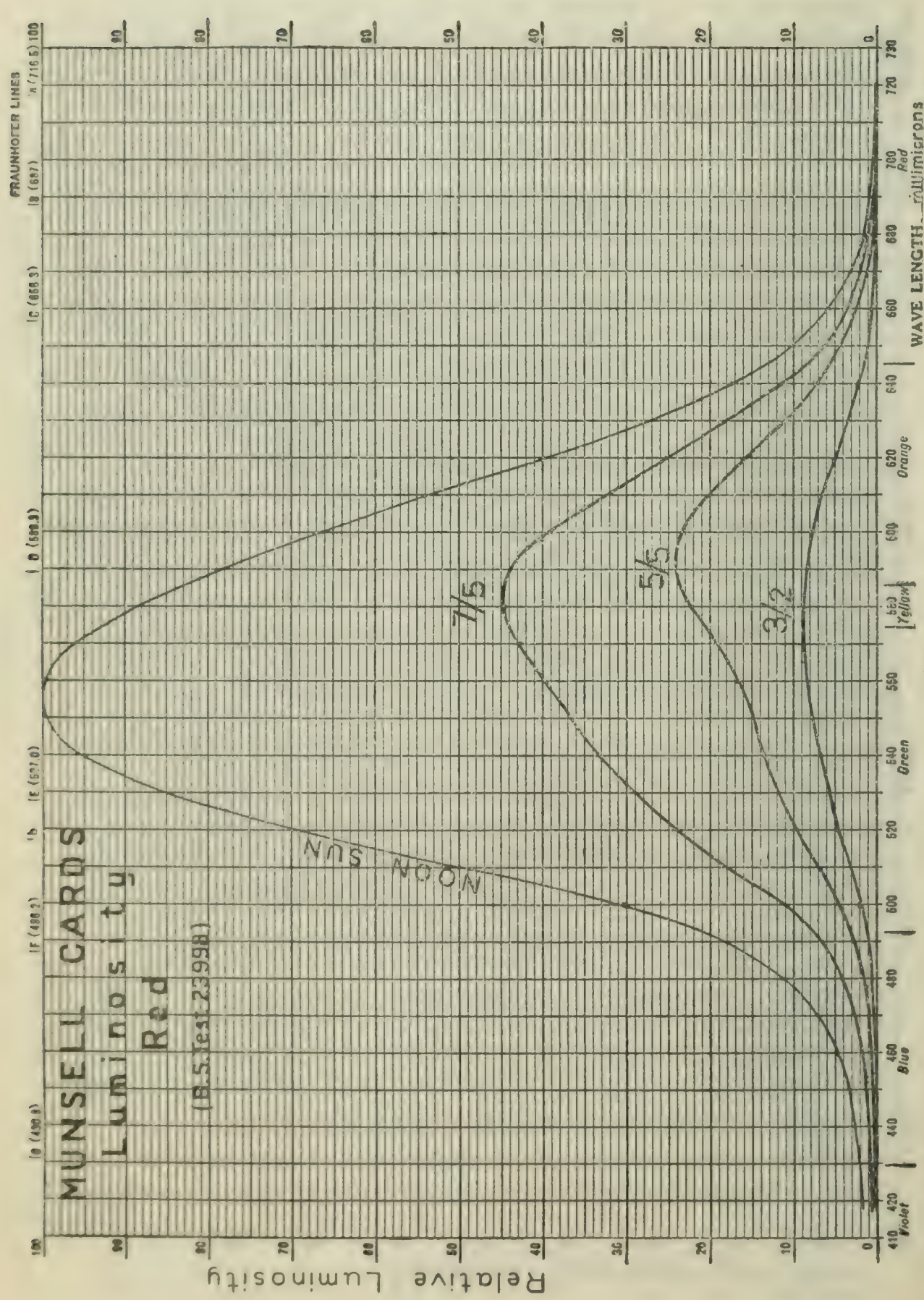

MUNSELL CARDS
Luminosity
Red
(B.S. Test 23998)
SUN NOON
7/5
5/5
3/2
Relative Luminosity
WAVE LENGTH—millimicrons
FRAUNHOFER LINES
Violet
Blue
Green
Yellow
Orange
Red

FIG. 9

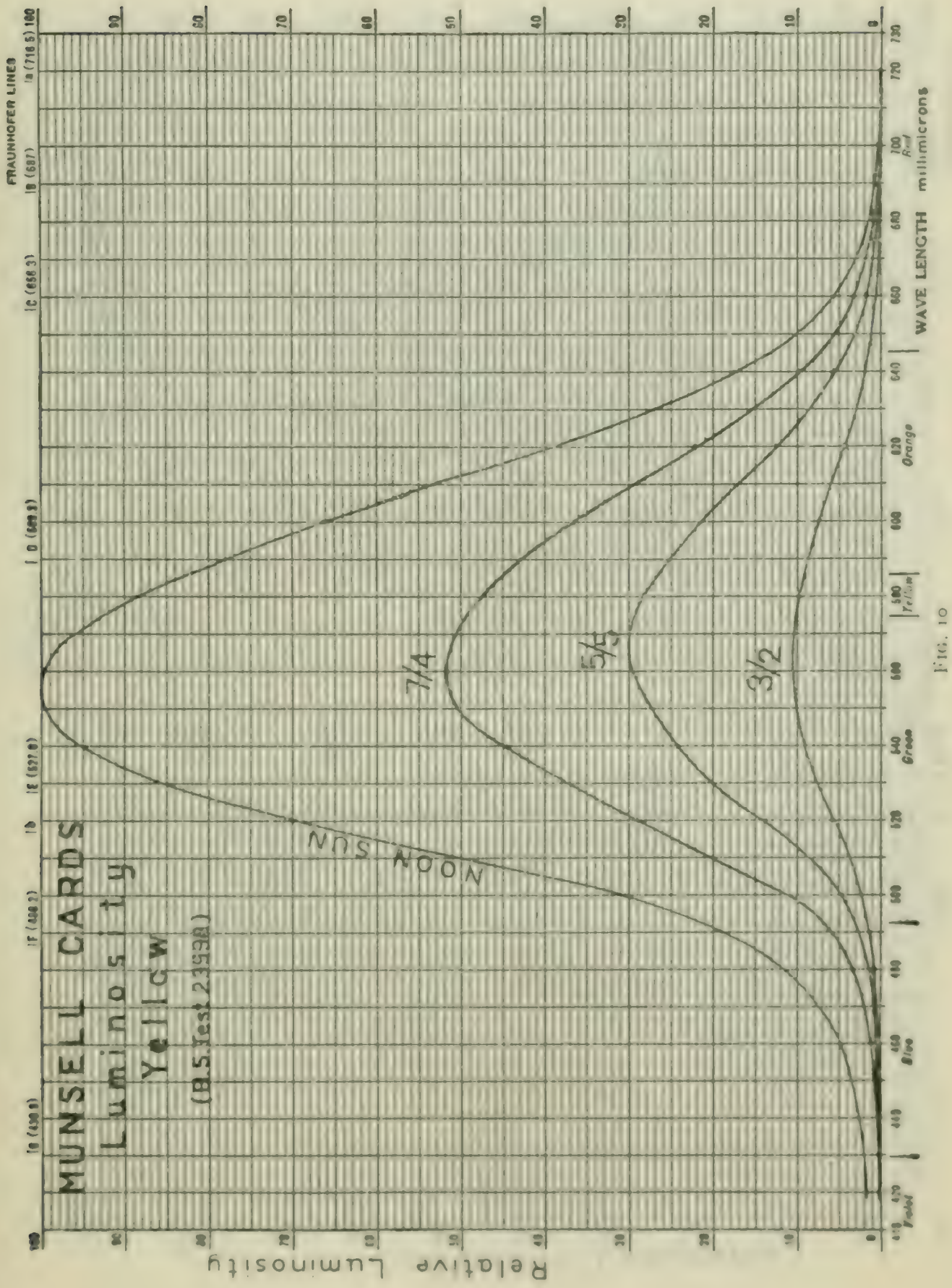

MUNSELL CARDS
Luminosity
Yellow
(B.S. Test 23938)
NOON SUN
7/4
5/4
3/2
WAVE LENGTH millimicrons
Relative Luminosity
FRAUNHOFER LINES

FIG. 10

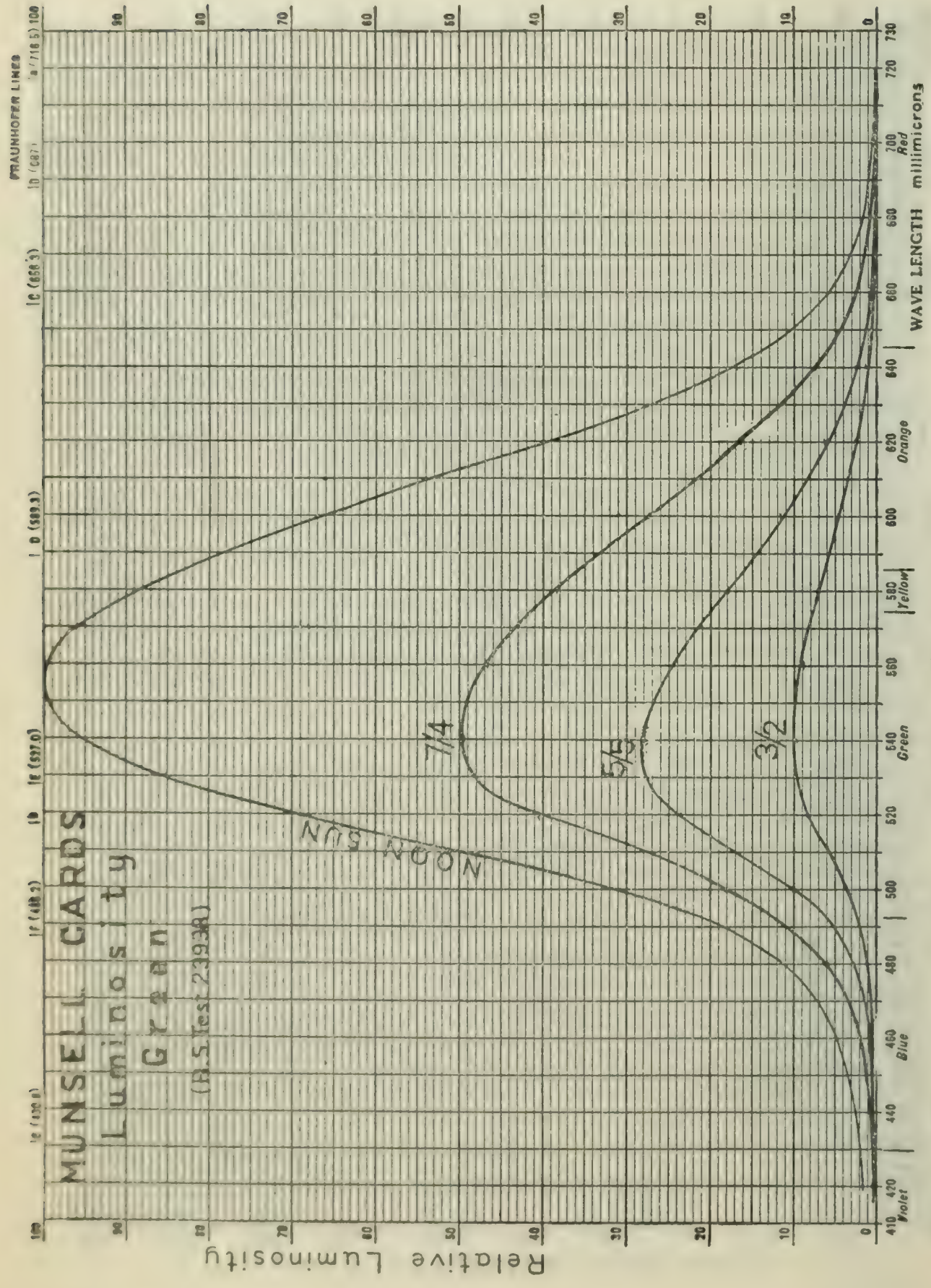

MUNSELL CARDS
Luminosity
Green
(B.S.Test 23938)
NOON SUN
7/4
5/2
3/2
Relative Luminosity
WAVE LENGTH millimicrons
FRAUNHOFER LINES
Violet
Blue
Green
Yellow
Orange
Red

FIG. 11

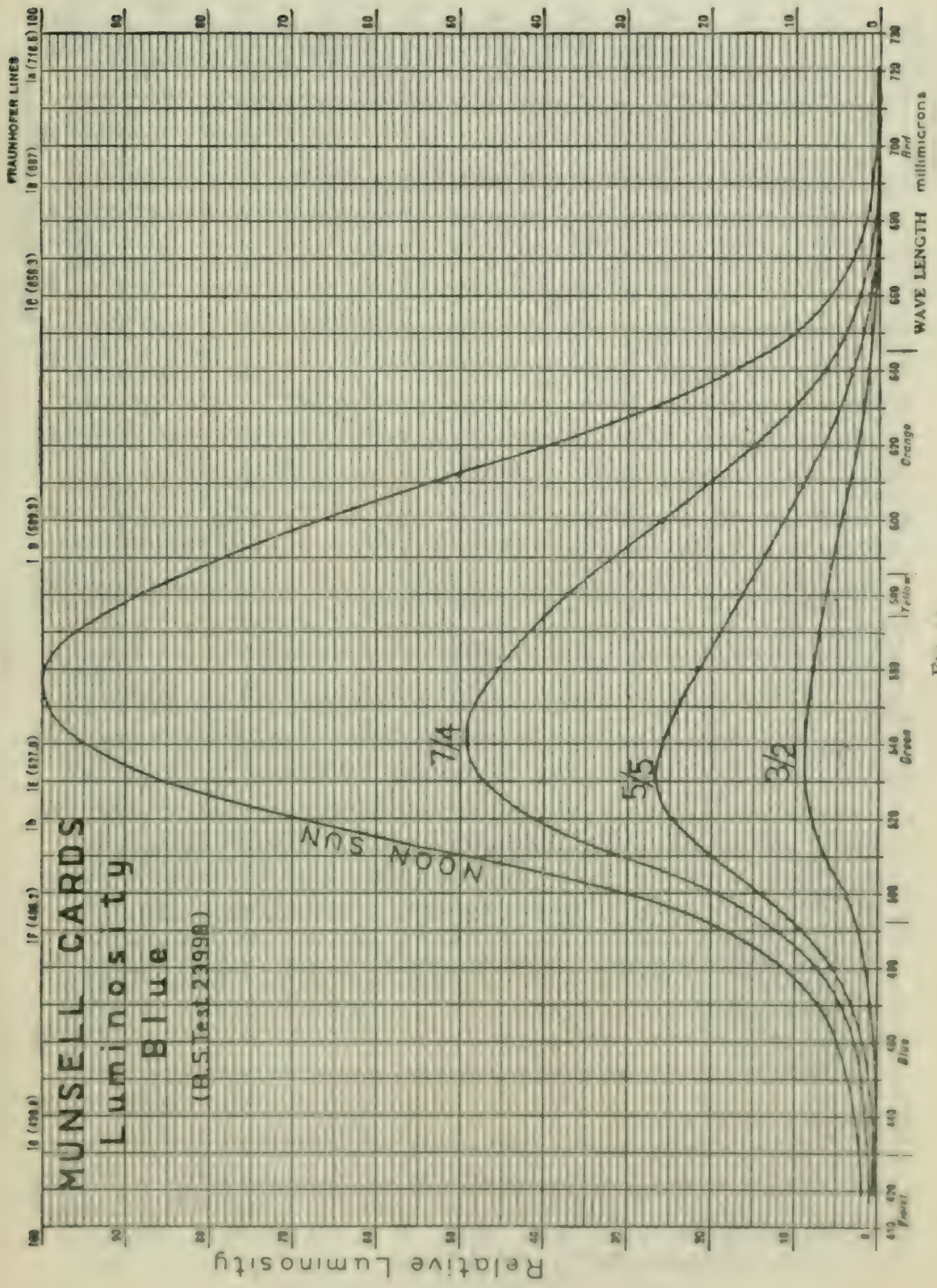
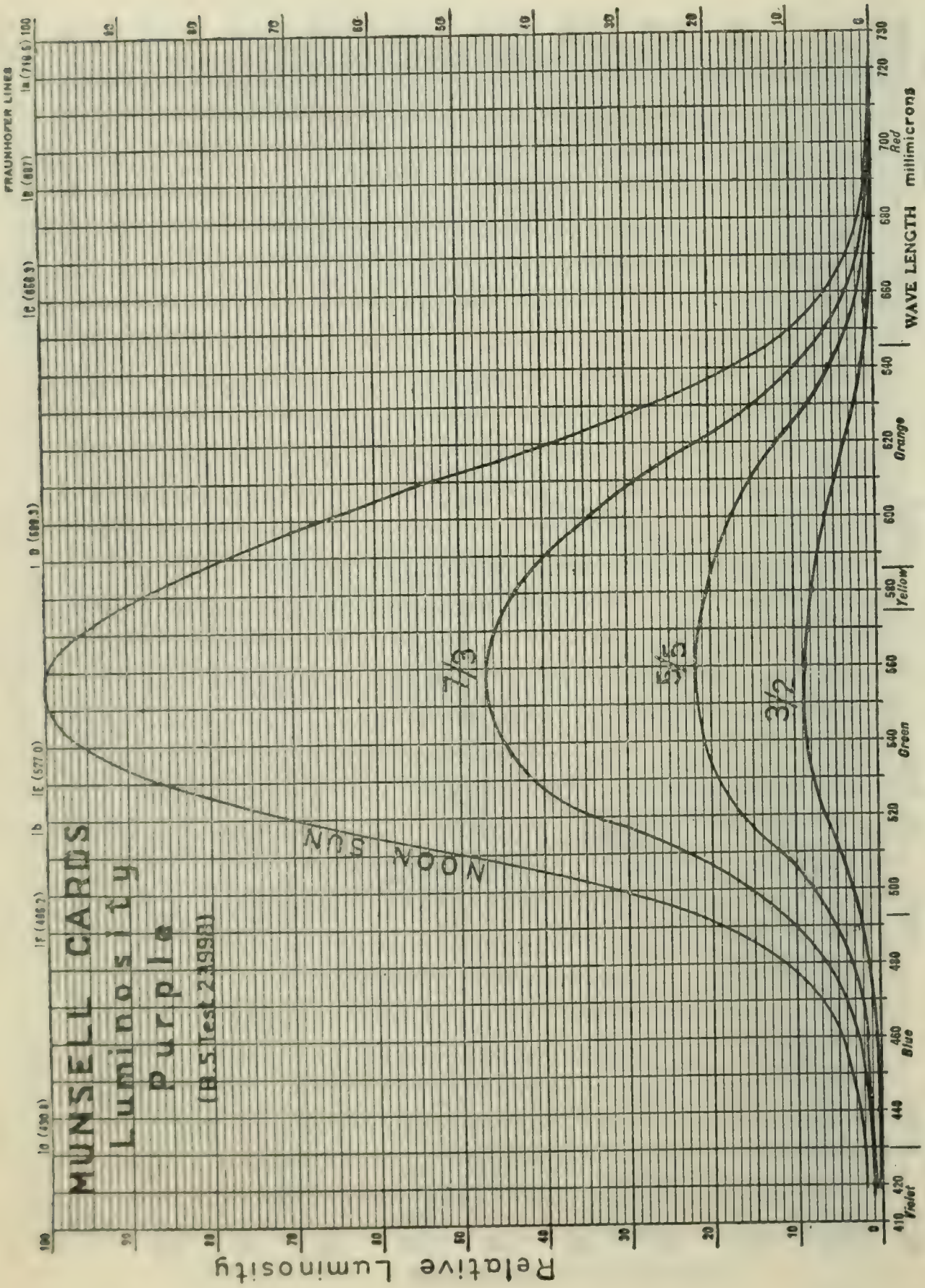

MUNSELL CARDS
Luminosity
Blue
(B.S.Test 2399B)
NOON SUN
7/4
5/5
3/2
WAVE LENGTH millimicrons
Relative Luminosity
FRAUNHOFER LINES

FIG. 12


MUNSELL CARDS
Luminosity
Purple
(B.S.Test 21558)
SUN NOON
7/6
5/6
3/2
Relative Luminosity
WAVE LENGTH millimicrons
FRAUNHOFER LINES
Violet
Blue
Green
Yellow
Orange
Red

(See Figs. 8 to 13, inclusive.) Such curves are known as spectral luminosity curves. Moreover, the area of this curve [15] divided by the area of the sunlight curve gives the total reflection of the card for sunlight. The total sunlight reflections obtained by this method, the areas having been measured with a planimeter, are shown in Table 3.

**TABLE 3.—Diffuse Reflection for Sunlight Relative to Magnesium Carbonate**

| | Gray | Red | Yellow | Green | Blue | Purple |
|---|---|---|---|---|---|---|
| Number | N 9 | | | | | |
| Reflection | 0.722 | | | | | |
| Number | N 8 | | | | | |
| Reflection | .602 | | | | | |
| Number | N 7 | R 7/6 | Y 7/6 | G 7/4 | B 7/6 | P 7/8 |
| Reflection | .465 | 0.451 | 0.488 | 0.477 | 0.476 | 0.496 |
| Number | N 6 | | | | | |
| Reflection | .343 | | | | | |
| Number | N 5 | R 5/6 | Y 5/6 | G 5/6 | B 5/6 | P 5/8 |
| Reflection | .234 | .222 | .270 | .239 | .249 | .242 |
| Number | N 4 | | | | | |
| Reflection | .161 | | | | | |
| Number | N 3 | R 3/2 | Y 3/2 | G 3/2 | B 3/2 | P 3/2 |
| Reflection | .090 | .087 | .100 | .091 | .095 | .089 |
| Number | N 2 | | | | | |
| Reflection | .041 | | | | | |
| Number | N 1 | | | | | |
| Reflection | .018 | | | | | |

Now, the Munsell value numbers are obviously some function of this total reflection. Indeed, it is explicitly stated on the charts in the Munsell Atlas that these numbers indicate the reflection of the cards in the sense that 1 means that 10 per cent of the incident light is reflected; 2 means 20 per cent; 3, 30 per cent; etc. *The results of our measurements, as given in Table 3, show conclusively that these statements in the Atlas are in error, and that the Munsell value numbers have no directly proportional relation to the reflections.* The actual relation existing between the Munsell values and the reflections is shown graphically in Fig. 14. From this curve one may read the reflection of sunlight corresponding to any Munsell value.

A very simple relation has been found to exist between the Munsell values and the reflections, *viz., the squares of the Munsell value numbers are directly proportional to the reflection of sunlight.* (See Fig. 15.) It seems likely that this relation has

[15] Included between the curve and the wave-length axis.

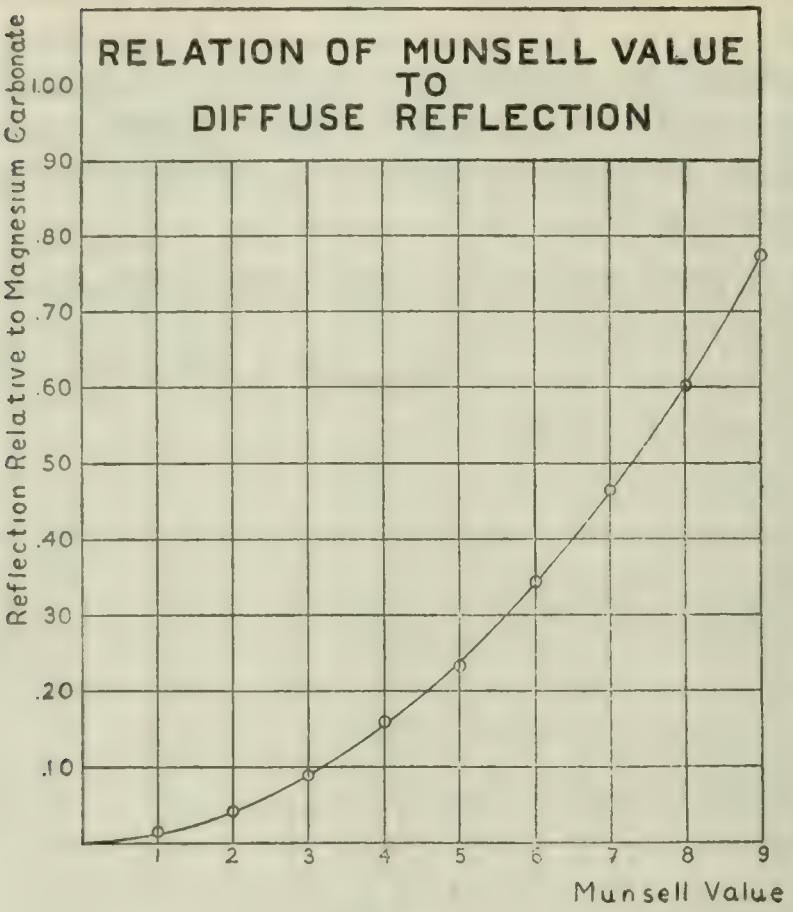

RELATION OF MUNSELL VALUE
TO
DIFFUSE REFLECTION
Reflection Relative to Magnesium Carbonate
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
1
2
3
4
5
6
7
8
9
Munsell Value

FIG. 14

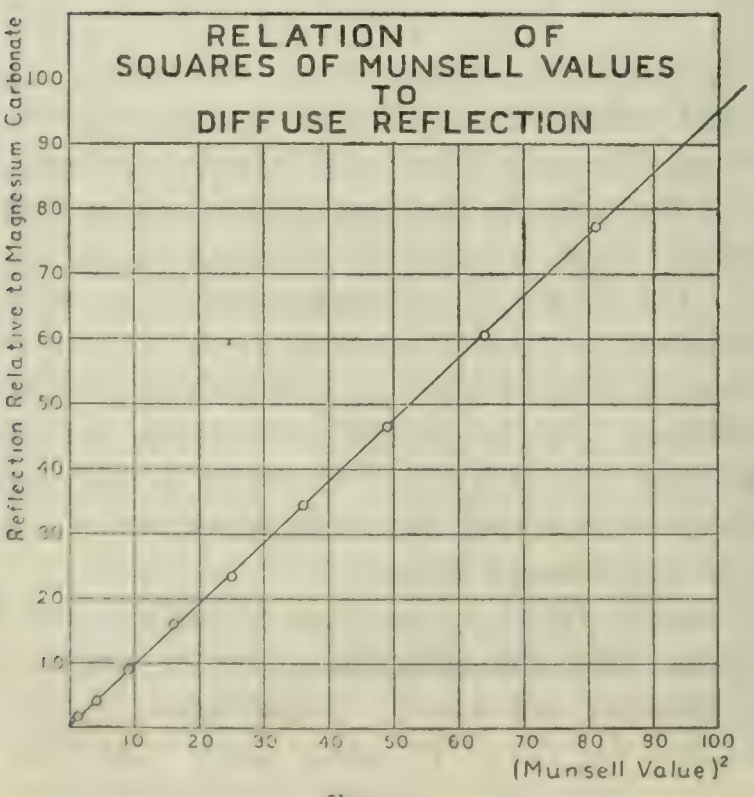

RELATION OF
SQUARES OF MUNSELL VALUES
TO
DIFFUSE REFLECTION
Reflection Relative to Magnesium Carbonate
100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
(Munsell Value)²

FIG. 15

been introduced into the system by an oversight in the use of the Munsell photometer.[16] Taking values as directly proportional to the diagonal of the opening of the diaphragm (valve) in the instrument would lead to just this result, for the reflection by the sample is evidently proportional to the square of this diagonal.

Whether this relation of value to actual light reflection was selected purposely or inadvertently by Munsell is not quite clear.[17] We may be sure that, as an artist, he would not have been satisfied with a value scale in which the reflections of the successive steps actually formed an arithmetical series, as 10 per cent, 20 per cent, 30 per cent, 40 per cent, etc. (even though it is stated in the Atlas that this is the interpretation of the value scale), for in such a scale the apparent contrast of different intervals would not be equal; for example, the contrast between 10 per cent and 20 per cent would be much greater than between 80 per cent and 90 per cent.

It will probably be agreed by all who are interested in the subject and consider it carefully, that the steps in the value scale should be apparently equal; that is, the visual contrast between the cards of any two adjacent numbers should equal that between any other adjacent two. Now, there is a well-known natural law which enables us to formulate mathematically (at least to a good approximation) the relation which must exist between the reflections of the members of the series of values in order that this condition may be satisfied. A scale conforming to this law may be called a natural value scale. This law may be stated in several forms, but probably the simplest and most

[16] Munsell Color Notation, Second Ed., pp. 57–58.

[17] In an advertising circular issued by A. H. Munsell and entitled, "The New Munsell Photometer (patented Nov. 19, 1912)," etc., we find the following paragraph:

"Intermediate positions of the shutter give *a regularly increasing scale of light from black to white—self registered on a dial* at the back wall by a gear shaft and index hand. The dial registers 100 when the shutter is open and 0 when it is shut, the intermediate degrees following Fechner's law of sensation. This calibration is easily verified, by comparing the area of opening at any position of the shutter, with the corresponding reading on the dial."

This paragraph is, however, covered by a pasted insert which reads as follows:

"The dial bears two scales, the inner of which may be used for comparing the intensity of light sources. Thus, with a standard 100-c.p. lamp opposite the fixed hall, and a 400-c.p. lamp opposite the variable hall, the shutter is clocked down to one-fourth its full area to procure a balance. The outer scale differs from the usual photometric scale in that it measures *sensations* of light rather than intensity. It is divided into 100 equal values (sensations of increase of luminous *y*), from complete blackness (0), to pure white illuminated to the full extent of the instrument. These sensation values read directly as the diagonal of the variable shutter in millimeters, and are used in this description."

The treatment here is somewhat more definite than in the "Color Notation" and apparently verifies our previous conclusion that Munsell values are directly proportional to the diagonals of the shutter openings. However, the whole treatment of the photometer and its use in measuring value is rather indefinite, and the implication that values, read directly as the diagonal of the shutter, are proportional to sensation in the sense of Fechner's law is quite wrong.

easily comprehended is: The reflections of the various members of the series of cards should form a geometric series; that is, the ratio of the reflections of any two adjacent cards in the series should be constant throughout the series.[18] This leads to a simple graphical relation which must exist between the value-scale numbers and the reflections; viz, the graph relating the value-scale numbers and the logarithms of the reflections must be a straight line. (See Fig. 16.) In this figure the logarithms of the measured reflections of the Munsell cards are plotted against their Munsell value numbers (dashed curve). It appears that while considerable parts of this curve are sensibly straight, it does not conform rigorously to the law stated above. *The curve indicates that the lower intervals of the Munsell scale are two great relative to the higher intervals. In our opinion this conclusion is verified by qualitative examination* of the cards submitted and tested. The lower intervals, 1–2, 2–3, 3–4, 4–5, look greater than the higher intervals, 5–6, 6–7, 7–8, 8–9.

However, the Munsell scale approximates much more nearly to the natural scale than a scale in which the reflections of the series form an arithmetical series. In Fig. 16 the dotted curve shows the relation between value numbers and the logarithms of reflections for a series of cards having the same end members as the Munsell cards but assumed to have their reflections in an arithmetical series. It will be noted that this curve departs much farther from a straight line than the Munsell curve. We may, perhaps, assume that Munsell, fully realizing the unsuitability of a value scale with reflections in arithmetical series, adopted his scale merely from artistic considerations and really approximated to the true natural scale of value by adopting his value numbers as proportional to the square roots of the reflections.

*Our sunlight reflections for the different hues given in Table 3 verify in a remarkable manner the consistency of the Munsell values for different hues.* It will be noted that the reflections for sunlight are nearly constant for the same Munsell values for all the hues and the neutral. Considering the uncertainties of heterochromatic photometry which were necessarily involved in Munsell's work, it seems remarkable that he obtained such consistent results for the values of different hues.

[18] This relation is based on Weber's law, often erroneously called Fechner's law. See Webster's International Dictionary, 1910 ed., under "Weber's law," and "Fechner's law." See also Ostwald, Farbenfibel, Leipzig, pp. 9–10, 1917. Külpe, Outlines of Psychology, Eng. Trans. by Titchener, p. 142; 1901.

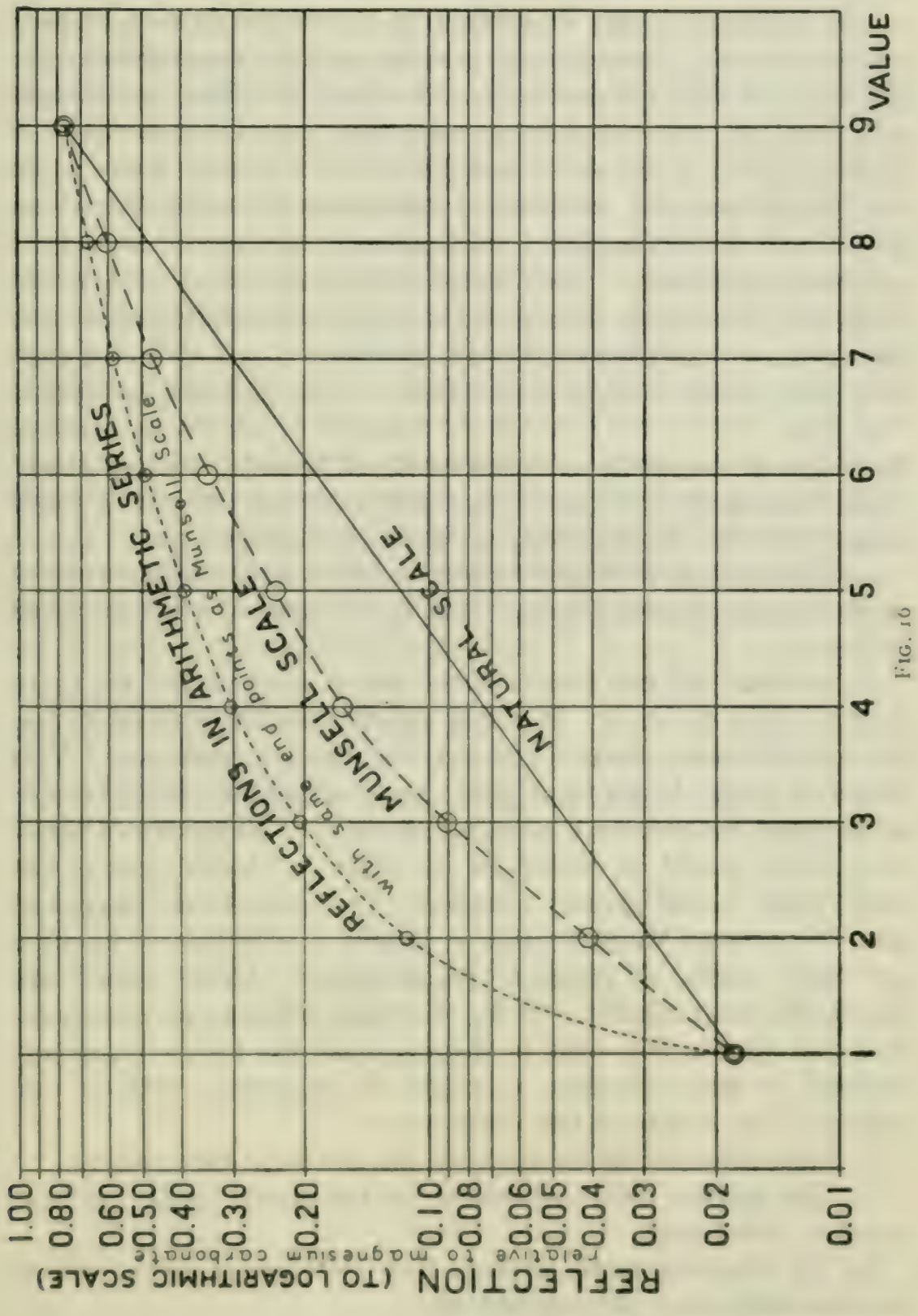

VALUE
9
8
7
6
5
4
3
2
1
NATURAL SCALE
MUNSELL SCALE
ARITHMETIC SERIES
Munsell Scale
REFLECTIONS IN
points as
and
same
with
REFLECTION (TO LOGARITHMIC SCALE)
relative to magnesium carbonate
1.00
0.80
0.60
0.50
0.40
0.30
0.20
0.10
0.08
0.06
0.05
0.04
0.03
0.02
0.01

FIG. 16

## V. PROPOSALS FOR THE IMPROVEMENT OF THE SYSTEM AND ITS ESTABLISHMENT UPON A MORE RELIABLE FOUNDATION

It is obviously highly desirable that a standard system, at least similar to that of Munsell in its general outlines, be established for the use of artists, art students, and others, including the makers and users of paints and inks, and other colored materials. A revised edition of the Atlas and The Color Notation, based upon the best present-day methods of measurement and specification, would be a most important contribution to the science and art of chromatics generally. That the production of such a work would be an enormous task, involving the hearty cooperation of artists, scientists, and practical colorists, is obvious; and it is not now clear just how it may be undertaken. It is, however, an opportune time to point out some of the features which, in our opinion, should be given careful consideration. Pending a further study of all the phases of the problem, these proposals can not be made exhaustive, but the following occur to us at present:

1. The value scale should be one in which the reflections of the cards form a geometric series; that is, the natural scale discussed above.

As to what the end points of the actual scale should be, there may be some question. It would appear reasonable to make 100 per cent absolute reflection one end of the scale (value=10). This would of course be an ideal limit, never attainable, but desirable as the ideal end reference point for the sake of simplicity of ideas. As to what should be chosen for the other or "black" end of the scale, there is still greater question. It is tentatively suggested that the present Munsell value 1, having a reflection of about 2 per cent, meets all practical requirements. Lower values are practically unattainable. It is, of course, obvious on consideration that we can not, even in theory, make the lowest value correspond to zero reflection, as might be suggested, without due regard to the nature of the value scale.

2. Each color should be specified physically in three ways:

(*a*) By spectral reflection curves (of the actual cards), such as given in this report.

(*b*) By monochromatic analysis,[19] *on the basis of an established standard white* (not yet established).

[19] Nutting, B. S. Bulletin, 9, p. 1; 1913.

(*c*) By its constants under prescribed conditions on the Arons chromoscope.[20]

3. The colorimetric and photometric specifications of the cards should accompany the Atlas, and should refer in clear terms to fundamental standards about which there can be no ambiguity.

4. Relative reflection or value measurements on different colors must be made with light of specified quality, and for this purpose it is reasonable to select average noon sunlight. Measurements of value can be made with the greatest convenience and reliability by means of the Martens photometer [21] and a hollow hemisphere arranged to illuminate the samples with diffuse light.[22] By a slight addition to the Martens photometer, it may be made to give true standard sunlight values, using gas-filled tungsten lamps as light sources. This can be accomplished by inserting between the eye and the present nicol prism in the instrument a quartz plate and another nicol.[23]

5. In order to avoid further confusion of terms, it would be highly desirable to secure a general agreement in nomenclature among those experts interested in this subject, before issuing another edition of this work. Steps toward the general standardization of the nomenclature of colorimetry are now being taken by the Bureau of Standards and the Optical Society of America.

WASHINGTON, November 11, 1919.

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[20] Ann. der Phys. (4), 39, p. 845; 1912.

[21] Phys. Zeit., I, p. 229, 1899.

[22] C. Lukesh, "Measurement of Reflection Factor," Electrical World, May 19, 1917.

[23] Priest, Phys. Rev. (2), 11, p. 502, June, 1918.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 168

# COLOR AND SPECTRAL COMPOSITION OF CERTAIN HIGH-INTENSITY SEARCHLIGHT ARCS

BY

IRWIN G. PRIEST, Physicist
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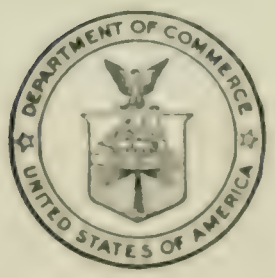
H. J. McNICHOLAS, Assistant Physicist
*Bureau of Standards*

AUGUST 12, 1920

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1920

# COLOR AND SPECTRAL COMPOSITION OF CERTAIN HIGH-INTENSITY SEARCHLIGHT ARCS

By Irwin G. Priest, W. F. Meggers, K. S. Gibson, E. P. T. Tyndall, and H. J. McNicholas

CONTENTS

| | Page |
|---|---|
| I. Introduction | 3 |
| II. Color measurements by rotatory dispersion colorimeter | 3 |
| III. Spectrophotometric measurements | 4 |
| IV. Spectroscopic analysis | 11 |

## I. INTRODUCTION

The development of high-intensity arcs by the use of specially prepared carbons has resulted in the production of a light which is very blue relative to artificial incandescent sources. In a general investigation of searchlights, including the effectiveness and suitability of their illumination for various purposes, it appeared desirable to have at least approximately quantitative data on the color of this light.

An investigation was made with the cooperation of the Searchlight Investigation Section, Corps of Engineers, U. S. Army. A report was issued to the Corps of Engineers and others January 23, 1919. Another report was made to the American Physical Society, April 25, 1919.[1] These reports are combined in the present paper.

The result of these investigations may be roughly summarized in popular language by saying that the color of the light from these arcs is approximately equivalent to the light of the noon sun at Washington, although relatively more intense in the blue-violet.

## II. COLOR MEASUREMENTS BY ROTATORY DISPERSION COLORIMETER

There are considerable difficulties in the spectrophotometry of a source such as the high intensity arc. It was therefore decided to obtain some preliminary data by the short cut color matching

[1] Phys. Rev. [illegible] 14, p. 151, August 1919.

method of rotatory dispersion.[2] By this method one may determine quickly a spectral distribution which gives the same color as the source studied. The spectral distribution for equivalent color of a Sperry 45-volt, 75-ampere searchlamp of the regular type supplied to the U. S. Army, obtained in this way, was found to be very close to that of the noon sun at Washington[3]; that is, approximately that of a "black body" at 6000° K. (See Fig. 7.)

## III. SPECTROPHOTOMETRIC MEASUREMENTS

Preliminary spectrophotometric measurements were made in April, 1918; but inasmuch as no description or specification of the carbons other than the maker's name was available, it was decided to make further measurements with carbons subjected to spectroscopic analysis for the sake of greater definiteness of description. These further measurements were made as follows:

The relative spectral distribution of radiant energy throughout the visible spectrum was measured for the following arcs:

| | Amperes |
|---|---|
| Sperry searchlight arc, Columbia carbons | 75 |
| Sperry searchlight arc, Speer carbons | 75 |
| Ordinary arc, Electra carbons | 10 |

These relative values of radiant power were obtained visually by a spectrophotometric comparison with a standard Mazda-C 500-watt lamp (B. S. Lamp No. 1717), whose relative radiant powers had previously been accurately determined radiometrically by W. W. Coblentz of this Bureau. The arrangement of the apparatus for this investigation is shown in Fig. 1.

The arc was inclosed in a sheet-iron box. One opening allowed the light to pass to the spectrophotometer, as shown, and a second, over which was a piece of Noviweld (shade 12) glass, enabled the operator to view the arc and thus exert the required control. The mechanism of the arc is such that both carbons are slowly rotated and advanced at a rate which keeps the distance between them constant. The positive carbon is horizontal, as shown, the negative carbon being in front and below (Fig. 3). The diaphragm shown in front of the positive carbon was 5 mm in diameter. In some of the observations it was used and in the others removed. It enabled measurements to be made on the central part of the positive carbon, the light from the outer

[2] Aron, Ann. der Phys., 39, p. 545, 1912; Priest, Phys. Rev. (2), 10, p. 208, 1917.
[3] Abbot's data. See Priest, Phys. Rev. (2), 11, p. 502; 1918.

portions and from most of the flame being excluded. The current through the arc was kept as near as possible to 75 amperes, a second operator controlling this current by means of an adjustable resistance.

When the standard lamp was in use, it occupied the same position as that given for the arc, this position being located by means of the total reflection prism and ground-glass focusing screen. The total reflection prism was, of course, removed while observations were being made. A second 500-watt Mazda-C lamp served as a comparison source. The voltages on these lamps were kept at constant values by means of a potentiometer and adjustable resistance, being 118 volts for the standard lamp and 125 volts for the comparison lamp. By means of suitable lenses, light from the two lamps, or from the arc and comparison lamp, was condensed and made to enter the two openings in the illumination box, which was fastened to the spectrophotometer support

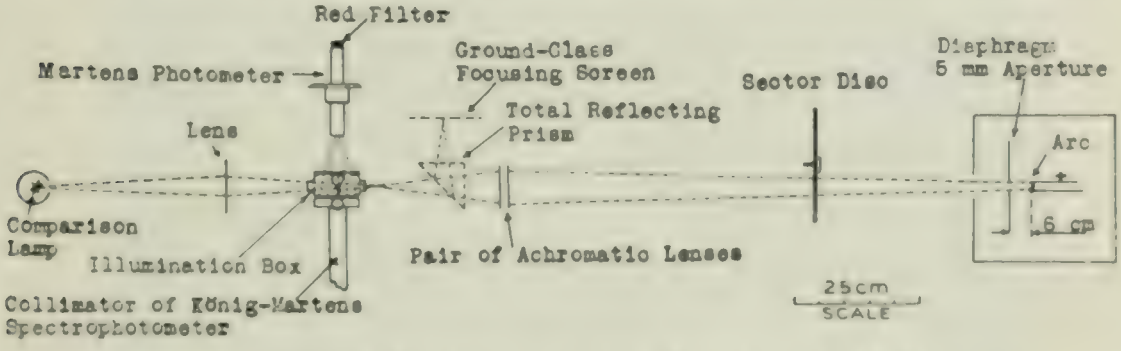



FIG. 1.—*Arrangement of apparatus for spectral comparison of light sources*

directly in front of the collimator slit. Errors due to chromatic effects from the lenses were avoided by using on one side a pair of achromatic lenses and on the other side only the light through the central part of the lens.

The details of the illumination box are shown in Fig. 2. The two compartments are separated from each other by a brass partition. The interior of each compartment was coated white with magnesium oxide put on by burning magnesium ribbon, and blocks of magnesium carbonate were placed as shown. Thus the whole interior was white and the reflection from all surfaces was entirely diffuse.

The magnesium carbonate blocks were illuminated as shown, and light from these two illuminated surfaces entered the double slit of the spectrophotometer through small openings in the illumination box. The whole interior of the box is, of course, illuminated by diffuse reflection from the magnesium carbonate blocks, and

two beams of light from the sides of the box next to the spectrophotometer pass through openings in the opposite side and are compared by means of the Martens photometer.

The Koenig-Martens polarization spectrophotometer [4] and the Martens polarization photometer [5] are essentially alike except for the dispersing prism. In brief, they operate as follows: Two beams of light are polarized mutually perpendicular, by means of a Wollaston prism, and brought together to form the two halves of a photometric field. This field is viewed through a nicol prism, and in this investigation the adjustments were such that the two halves of the field in either instrument were brought to equality by the analyzing nicol somewhere between 30 and 60° on the scale.

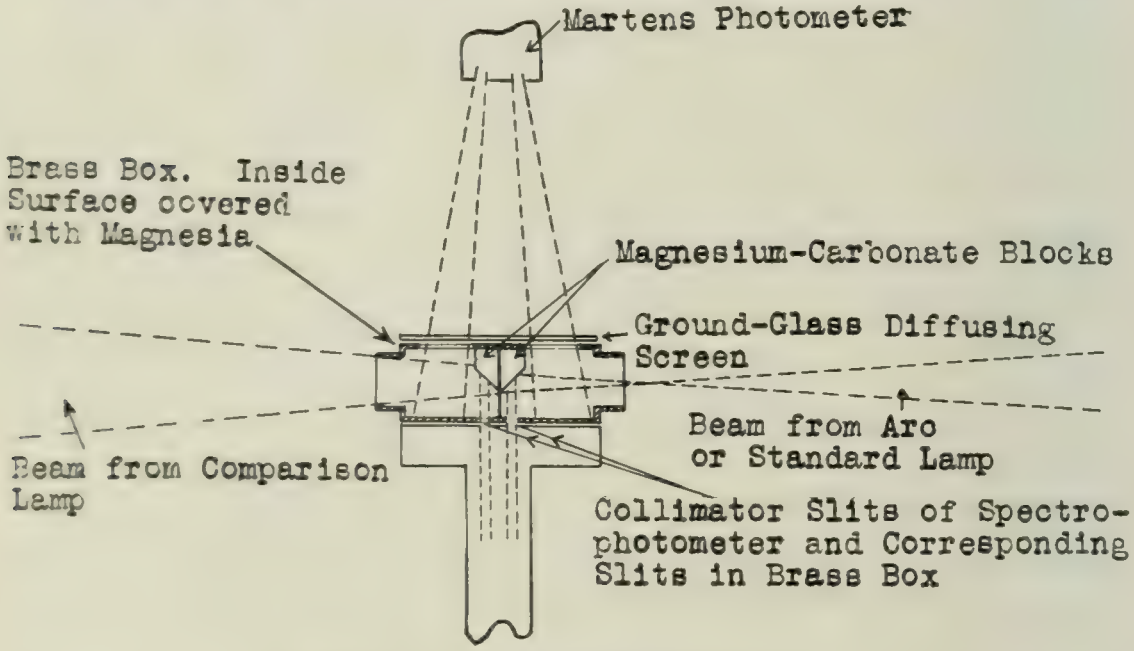

Martens Photometer
Brass Box. Inside Surface covered with Magnesia
Magnesium-Carbonate Blocks
Ground-Glass Diffusing Screen
Beam from Arc or Standard Lamp
Beam from Comparison Lamp
Collimator Slits of Spectrophotometer and Corresponding Slits in Brass Box

FIG. 2.—*Details of illumination box*

To bring this about, it was usually necessary to place a rotating sector in the beam of the arc when it was used and in the beam of the comparison lamp when the standard lamp was used. A red glass filter was placed over the eyepiece of the Martens photometer (Fig. 1) to eliminate the color difference between the arc and the comparison lamp, and a ground-glass diffusing screen used, as shown (Fig. 2), to make the photometric field still more uniform and of the proper brightness.

Five people were necessary in making the observations on the arc, one to watch and control the arc, recording the readings of the voltmeter; a second to regulate the current through the arc, recording the readings of the ammeter; a third to observe the

[4] Ann. der Phys. (4), 12, p. 984; 1903.
[5] Phys. Zeit., 1, pp. 299–303; 1900.

illumination through the Martens photometer; a fourth to take readings on the spectrophotometer; and a fifth to record those readings and keep the proper voltages on the lamps by means of the potentiometer. The procedure for taking a series of observations under these conditions was as follows:

The arc was allowed to run a few minutes in order that conditions might become as steady as possible. While this was being done, the comparison lamp was kept at its proper voltage and the variations of the illumination from the arc followed on the Martens photometer. Finally, the photometer was set for equality of brightness between the two sources at what seemed to be the best mean value of the illumination from the arc. This setting was

FIG. 3.—*The Sperry arc in operation, viewed in a direction perpendicular to the plane of the carbons. The positive carbon is horizontal. (Photo by Dr. Enoch Karrer)*

then unchanged during the run. Now, for any given wave length, the variations in the illumination from the arc were followed on the spectrophotometer, the attempt being made to keep the two halves of the photometric field always equal in brightness. Whenever conditions were right, as shown by the Martens photometer, a sharp signal was given and the reading of the spectrophotometer taken at that instant. It was not attempted to do this, of course, if the illumination varied too rapidly through the proper value. Usually the variations were quite slow, the illumination often staying constant at the correct value for a considerable part of a minute. It was noticed during the course of the investigation that the value of the current through the arc would have served nearly as well as the auxiliary photometer for enabling measure-

ments to be made always at the same illumination; for the current was practically always at a given value, about 75 amperes, when the signal was given by the observer at the Martens photometer.

At each wave length from four to ten readings were taken on the spectrophotometer, the number depending on the agreement obtained among the readings. Measurements were made between wave lengths 430 or 440 and 710 mμ, usually at every 20 mμ.

After this series of measurements was completed, the total reflection prism was set up to locate the position of the arc and kept there until the standard lamp had been put in position. It was then removed, and another series of measurements made at the same wave lengths as previously on the arc. Only two observers were now necessary, one to make the measurements on the spectrophotometer, the other to record the data and keep the voltages constant with the potentiometer.

In this manner all the data were obtained, either a complete run or check points being taken on the standard lamp between any two of the runs on the arc.

The spectral distribution of radiant power of the arc was computed as follows: All the values of the angles of the nicol prism read on the spectrophotometer for the standard lamp were plotted at the proper wave lengths and a smooth average curve drawn through these points. All values for the standard lamp used in the computations were taken from this curve. Thus the same values of the standard lamp were used for all computations. For each wave length the square of the cotangent of the average angle, read on the spectrophotometer when the arc was in position, was divided by the square of the cotangent of the angle as read from the curve when the standard lamp was in position. When this is done for all the wave lengths, the radiant power of the arc relative to that of the standard lamp is obtained. By multiplying these values by the known relative values of radiant power of the standard lamp at the different wave lengths, the relative spectral distribution of radiant power in the arc was obtained.

These values are plotted in Figs. 4 to 7, the legend in the figures making clear the interpretation of the data. The values of all curves are made 100 at 590 mμ.

There seems to be no consistent difference between the data for the Columbia carbons and for the Speer carbons. In both cases the values obtained when the diaphragm was used are lower in the blue than those found with the arc undiaphragmed.

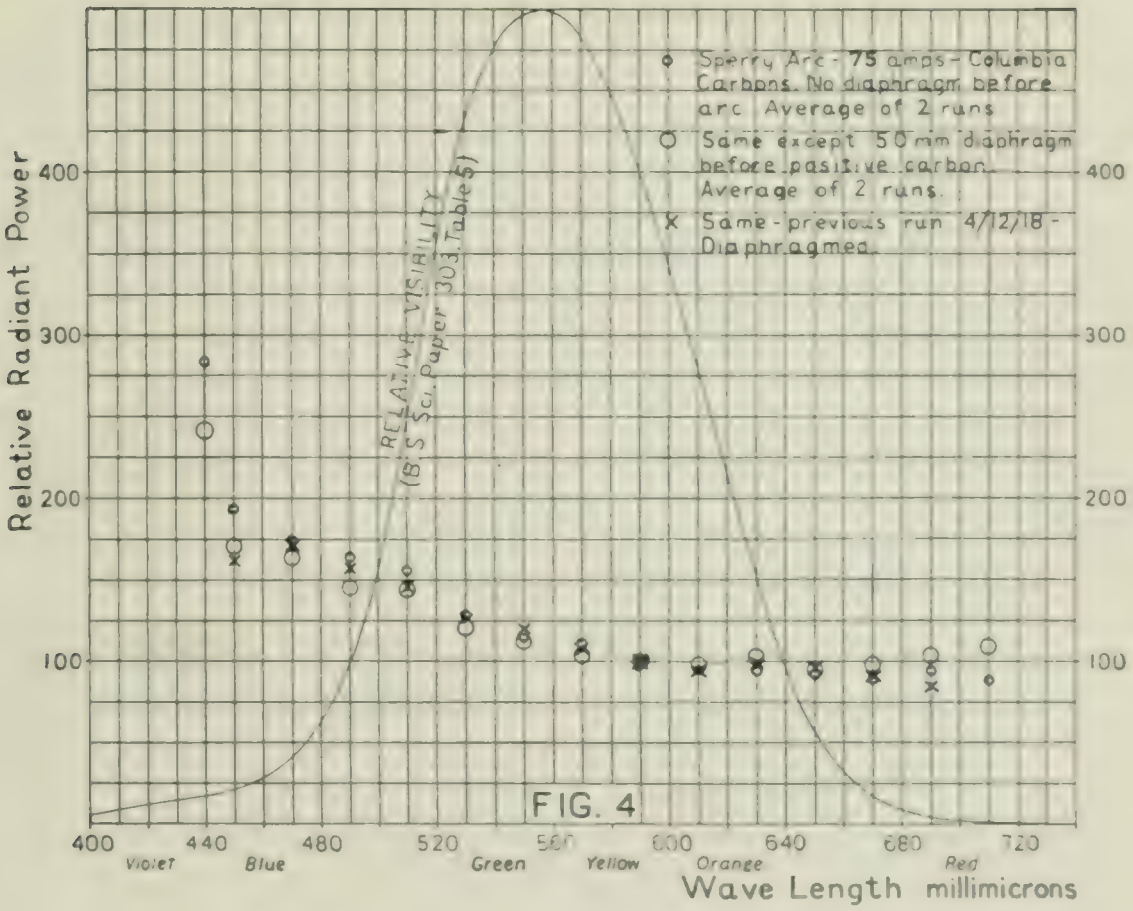

Sperry Arc - 75 amps - Columbia Carbons. No diaphragm before arc Average of 2 runs
Same except 5.0 mm diaphragm before positive carbon. Average of 2 runs.
Same - previous run 4/12/18 - Diaphragmed.
RELATIVE VISIBILITY (B.S.Sci. Paper 303. Table 5)
Relative Radiant Power
400
300
200
100
400 440 480 520 560 600 640 680 720
Violet Blue Green Yellow Orange Red
Wave Length millimicrons

FIG. 4

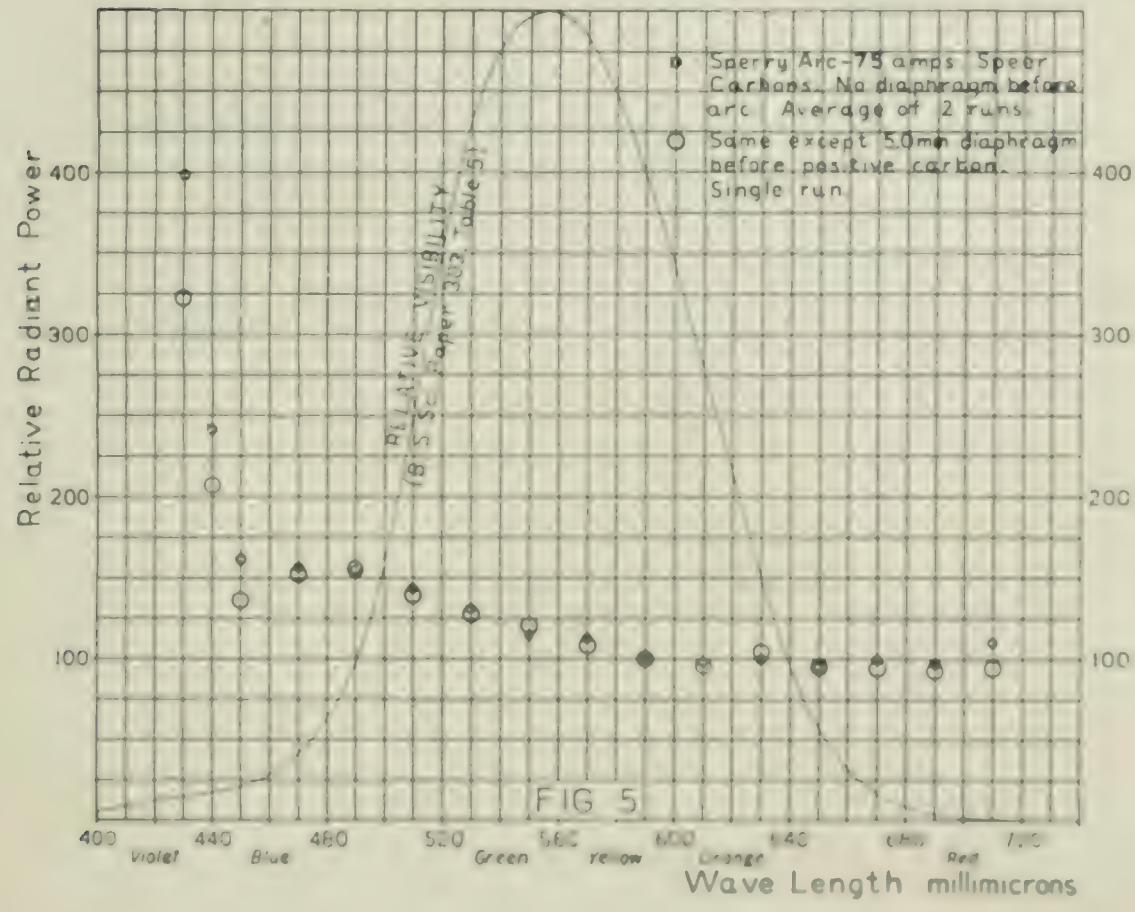

Sperry Arc-75 amps Speer Carbons. No diaphragm before arc Average of 2 runs
Same except 5.0mm diaphragm before positive carbon. Single run
RELATIVE VISIBILITY (B.S. Sci. Paper 303. Table 5)
Relative Radiant Power
400
300
200
100
400 440 480 520 Green Yellow Orange Red
Violet Blue
Wave Length millimicrons

FIG 5

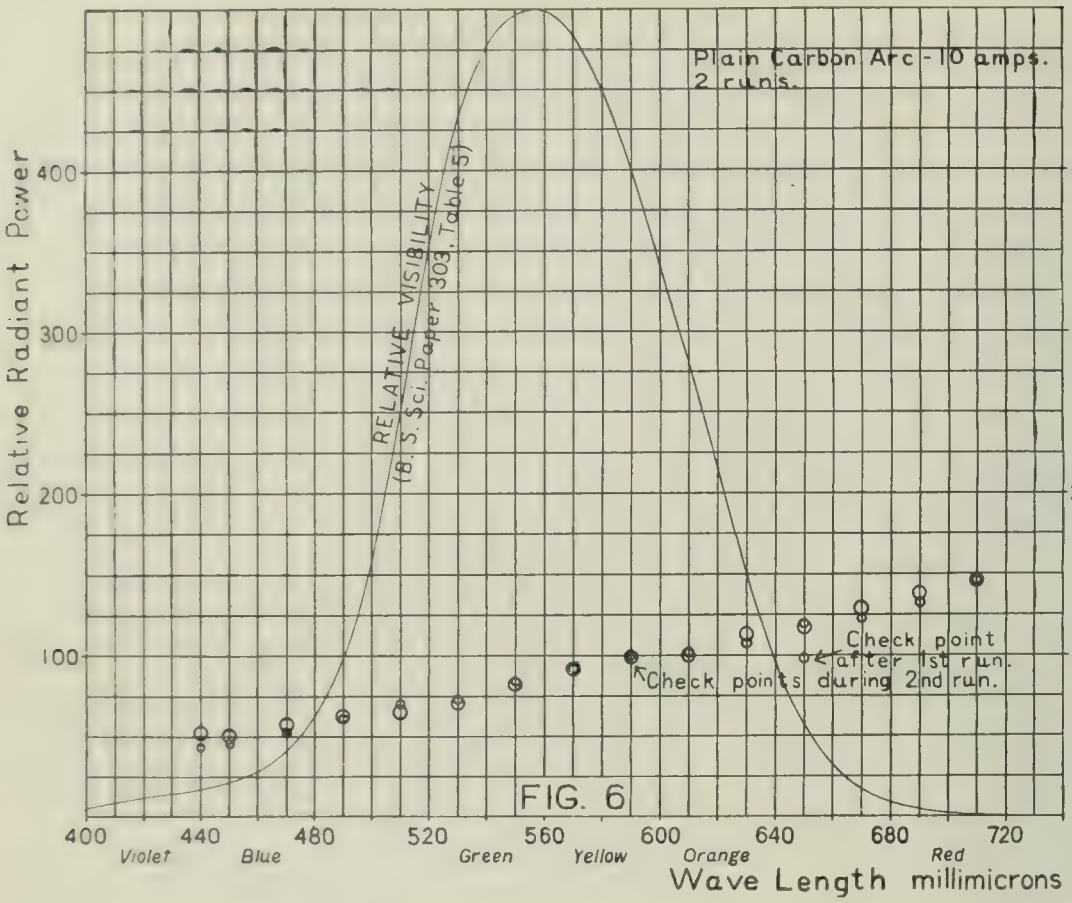

Plain Carbon Arc - 10 amps.
2 runs.
RELATIVE VISIBILITY
(B. S. Sci. Paper 303, Table 5)
Check point
after 1st run.
Check points during 2nd run.
Relative Radiant Power
100
200
300
400
Violet
Blue
Green
Yellow
Orange
Red
Wave Length millimicrons

FIG. 6

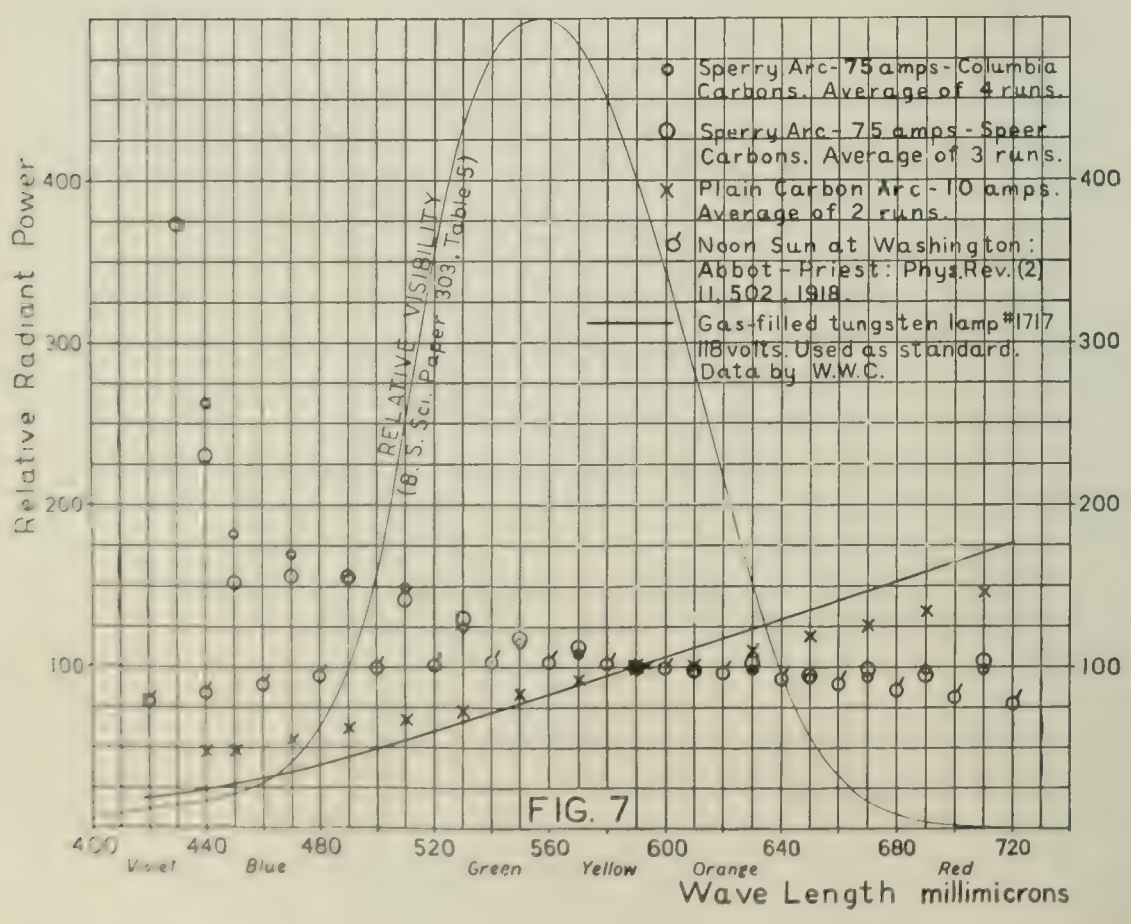

Sperry Arc - 75 amps - Columbia Carbons. Average of 4 runs.
Sperry Arc - 75 amps - Speer Carbons. Average of 3 runs.
Plain Carbon Arc - 10 amps. Average of 2 runs.
Noon Sun at Washington: Abbot - Priest: Phys. Rev. (2) 11, 502, 1918.
Gas-filled tungsten lamp #1717 118 volts. Used as standard. Data by W.W.C.
RELATIVE VISIBILITY
(B. S. Sci. Paper 303, Table 5)
Relative Radiant Power
100
200
300
400
Violet
Blue
Green
Yellow
Orange
Red
Wave Length millimicrons

FIG. 7

In the red, however, the diaphragmed values are higher than the undiaphragmed values in one case (Columbia carbons) and lower in the other (Speer carbons).

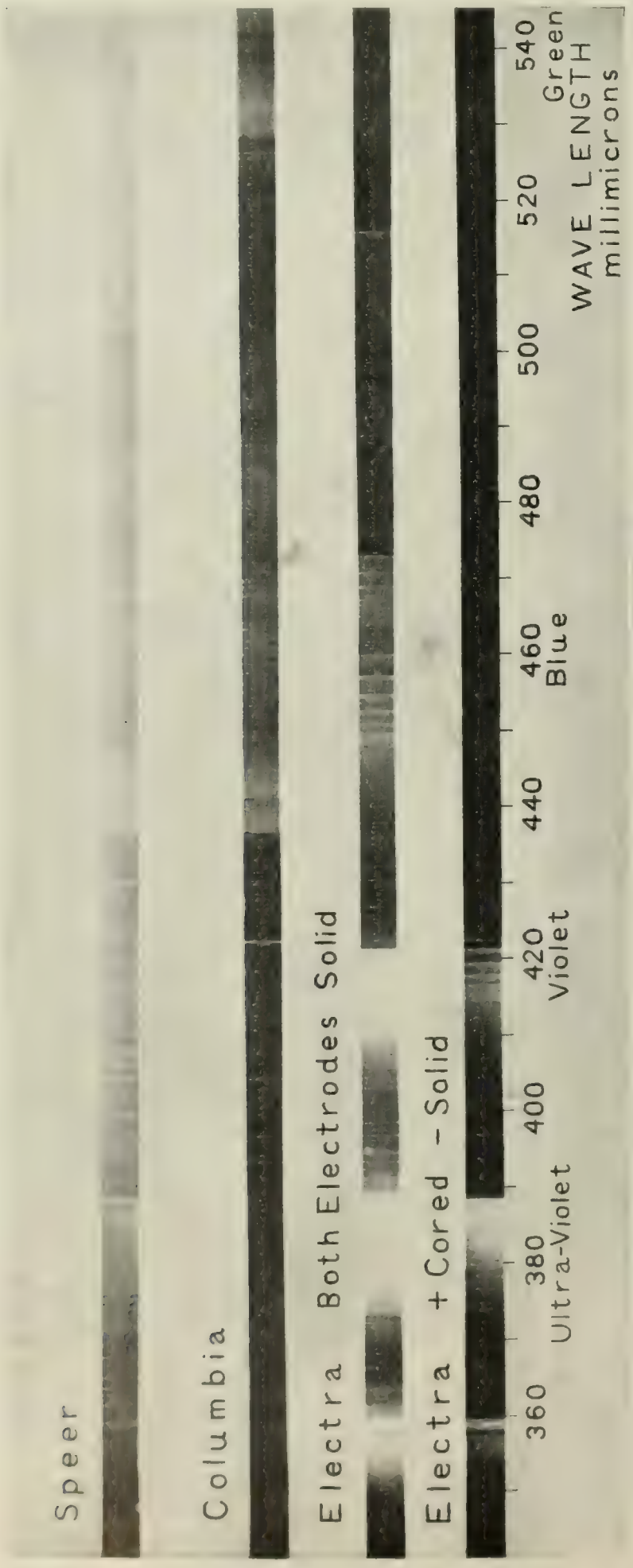
The curves for the plain carbon arc at 10 amperes show nothing unusual, except the low values at 610 mμ.

Perhaps the most striking characteristic of the spectral distribution of radiant power of the 75-ampere arcs is the preponderance of blue. This was to be expected from the bluish color of the arc when run at that current. The sudden increase of radiant power below 450 mμ is too large to be due to errors of measurement, in spite of the difficulty of obtaining accurate values in this region, and is undoubtedly due to a selective emission band in this region. (See Fig. 8.) Other irregularities in the 75-ampere curves which are thought to be real are the low values at 450 and the high values at 630 mμ. Other small irregularities in the curves are probably due to experimental error, although, considering the great number of bright lines in the spectrum, it may perhaps be considered surprising that an approximately smooth curve was obtained at all.

## IV. SPECTROSCOPIC ANALYSIS

Photographs of the spectra of these three kinds of carbons, the current in each case being 10 amperes, are shown in Fig. 8. The spectra were made with a large diffraction grating, using light from the center of the arc stream so that the line spectra characteristic of the metals in the vapor could be photographed, while the spectrophotometric measurements were made mainly on light from the central part of the positive pole which gives a continuous spectrum with bright lines superposed. The spectrograms, made for the purpose of defining the chemical constitution of the carbon electrodes, therefore have little relation to the spectrophotometric observations.

Spectroscopic analysis revealed the fact that the Columbia and Speer carbons were cored with a mixture of rare earth elements, among which cerium, thorium, lanthanum, and yttrium were represented. The emission spectra of these rare earths are very rich in lines, especially in the blue and violet spectral regions, so that a combination of them gives practically a continuous spectrum. Spectroscopic analysis of the incandescent vapors in the center of the arc showed that the rare earths in the Columbia and Speer carbons carried most of the current and suppressed the


Speer
Columbia
Electra Both Electrodes Solid
Electra + Cored - Solid
360
380
Ultra-Violet
400
420
Violet
440
460
Blue
480
500
520
540
Green
WAVE LENGTH
millimicrons

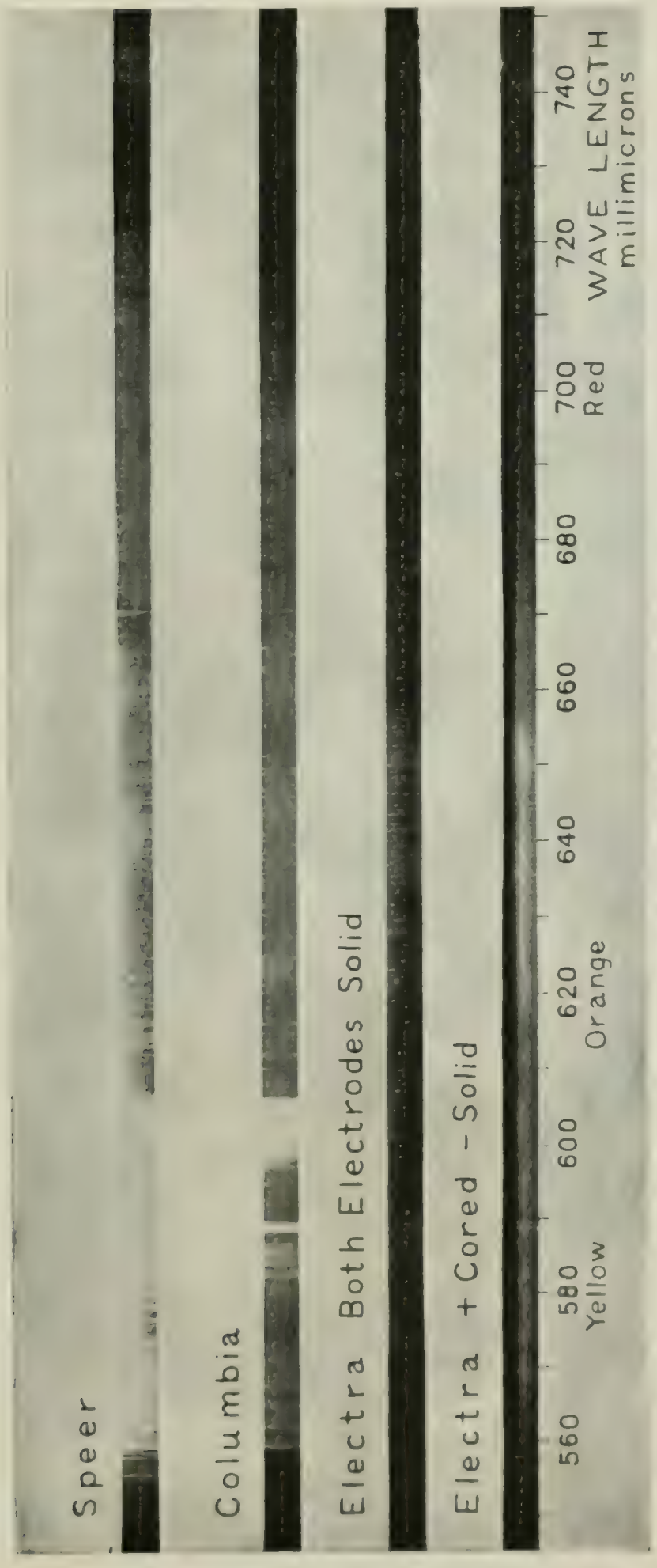



FIG. 8.—*Spectra of arcs at ten amperes*

spectrum of carbon, while the Electra carbons, which contained no rare earths, gave a very discontinuous spectrum in which the carbon bands of short wave lengths were most prominent.

Various circumstances have prevented extending and amplifying this work; and since there is no immediate prospect of opportunity to resume it, and there appears to be little authentic data available on this subject,[6] it is considered advisable to publish now the data which we already have.

It is also believed that the methods described above will be found useful by others for the investigation of light sources of the kind considered in this report.

WASHINGTON, October, 1919.

[6] Since this report was first written, some data attributed to Abbot have been published by Lichtenberg (Convention, Ill. Eng. Soc., Chicago, Oct. 20, 1919). It appears that these data are not entirely consistent with ours; but Lichtenberg's treatment of it in the advance copy of his paper received here is not sufficiently complete to enable us to judge what the actual discrepancy may be.

DEPARTMENT OF COMMERCE

# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 169

## MEASUREMENT OF PLASTICITY OF MORTARS AND PLASTERS

BY

WARREN E. EMLEY, Chemist

*Bureau of Standards*

JUNE 28, 1920

PRICE, 10 CENTS

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# MEASUREMENT OF PLASTICITY OF MORTARS AND PLASTERS

By Warren E. Emley

CONTENTS


| | Page |
|---|---|
| I. Introduction | 3 |
| II. Definition of plasticity | 5 |
| III. History of previous work | 7 |
| 1. Measurement of colloidal content | 8 |
| 2. Measurement of viscosity | 9 |
| 3. Compressive method | 12 |
| 4. Range of plasticity | 13 |
| 5. Rate of drying | 14 |
| 6. Carson blotter test | 15 |
| IV. Present instrument for measuring plasticity | 16 |
| 1. Operation | 17 |
| 2. Method of recording results | 19 |
| 3. Interpretation of results | 19 |
| 4. Numerical expression of results | 20 |
| 5. Adopted method of expressing results | 22 |
| V. Plasticities of miscellaneous materials | 23 |
| VI. Effect of consistency upon plasticity | 23 |
| VII. Effect of proportion of sand upon plasticity | 25 |
| VIII. Conclusion | 27 |


## I. INTRODUCTION

Everyone knows that plasters, mortars, clays, and certain other classes of materials are plastic. They must be plastic or they can not be used for the purposes for which they are intended. On the other hand, few people realize the enormous influence which the degree of plasticity has on the economic use of the material.

Take the case of wall plasters, for example. About 70 per cent of the total cost of plastering your house is accounted for by the labor required to spread the plaster on the wall. If one plaster is more plastic than another, it means that the plasterer can cover more square yards in a given time with the former than with the latter, which, of course, will reduce the cost. Furthermore, the more plastic material entails less physical and mental fatigue on the part of the plasterer, and he is thereby led unwittingly to produce a better quality of work.

The material used for the final coat of wall plaster must have plasticity in a very high degree. In fact, the requirements are so severe that neither Portland cement nor calcined gypsum can be used by itself for this purpose; a certain amount of lime must be added to give plasticity. This means that dealers must carry in stock and deliver on the job two materials, and the plasterer must mix these two materials, whereas if either cement or gypsum had the desired plasticity, one material would be sufficient.

While lime in general is more plastic than cement or gypsum, different limes have different degrees of plasticity. Any kind of quicklime, when properly slaked, will produce a putty of very great plasticity. Unfortunately this material is difficult to handle by inexperienced operators, so that the phrase "when properly slaked" is of undue importance. On the larger operations, especially in cities, hydrated lime is rapidly replacing quicklime as a plastering material, because of its greater convenience and the fact that it is already slaked. Hydrated limes are divided very sharply into two classes, on the basis of their plasticity—the "finishing" limes, made from a kind of limestone peculiar to a small district in northwestern Ohio, and all other hydrates. As the art of making hydrate is improved, it is probable that finishing hydrates will be made elsewhere. In fact, this result has already been achieved in one or two cases, to be noted later. The plasterer was quick to discover the difference between the two kinds of hydrate and to take advantage of it. The result is that either putty made from quicklime, or Ohio finishing hydrate, is always specified to be mixed with the gypsum for the final coat of plaster, with the tendency strongly in favor of the hydrate.

In 1915 Ohio finish was being sold in Los Angeles at $26 per ton, as compared with $14 for the locally made hydrate. The owner who is building a home in Los Angeles is fully cognizant of the meaning of plasticity as expressed in dollars and cents.

Many investigators have attempted to develop finishing hydrates outside of Ohio. Several attempts have been made to improve the plasticity of Portland cement and of calcined gypsum. These investigators have always been handicapped by the lack of reliable means for measuring plasticity. It was necessary to make experiments on a large scale, so that enough material could be produced to permit a plasterer to spread it on a wall. The opinion of the plasterer was then recorded as indicating the plasticity of the material. The opinion of any man as to the amount of work which he performed to accomplish a given result

is quite undependable. It will vary with his state of health and with his mental attitude, and the opinions of two individuals will seldom be found to agree. This method of procedure is therefore both unreliable and extremely expensive, so that most investigators have been compelled to abandon their researches without definite results.

Plasticity of a material is a property for which the consumer pays extra. The improvement of the plasticity of materials now on the market can readily lead to a saving of money to the consumer. For these reasons, the measurement of plasticity is not a question of academic interest only, but is of real practical importance to everyone who uses or pays for any mortar or plaster.

## II. DEFINITION OF PLASTICITY

It seems strange that a property so important and so generally well known as plasticity should be so difficult to define that it has become the subject of endless discussion. Everyone who has made no special study of the subject can tell whether or not a material is plastic. But when one does make a special study of plasticity, the definition which he evolves is apt to be colored by the application of the material with which he is dealing, or by the viewpoint from which his research was undertaken.

A broad general definition, states that "plasticity is that property of a material, or combination of materials, by virtue of which it deforms continuously and permanently during the application of force." [1]

Unfortunately, this is not sufficiently detailed for everyday use. Its greatest fault lies in the fact that plasticity so defined is not comparable. According to this definition, a material either is plastic or it is not; it can not be more or less plastic.

Engineers, who approach the subject from the viewpoint of a solid, emphasize the fact that the deformation of a plastic material must be permanent, in contradistinction to the deformation of an elastic material, which is not permanent.[2]

Other investigators, starting from the viewpoint of a viscous liquid, find that a plastic material will sustain a slight initial load without deformation, while a true liquid will not.[3]

The users of plastic materials have their own ideas on the subject, and these ideas differ with different trades. Thus, a

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[1] Report of Committee C-7, Amer. Soc. Test. Mat., 1919.

[2] Johnson, Materials of Construction, p. 1, 1915.

[3] Bingham and Green, Paint, a Plastic Material and not a Viscous Liquid, Proc. Am. Soc. Test. Mat., 1919.

clay worker may speak of a clay as being too plastic, whereas such a term would appear absurd to a plasterer.

To arrive at a definition which can be used to establish a basis of measurement, it seems necessary, therefore, to confine ourselves to the particular uses, as plasters and as mortars, of the plastic materials. If such a definition enables us to evolve a machine which will correctly measure plasticity, then it is highly probable that the same definition and machine can be used for materials other than plasters and mortars, even though such use may involve a readjustment of generally accepted nomenclature. If a machine which is designed to measure the plasticity of plasters will not also measure the plasticity of sands or clays, with only minor changes to enlarge its scale, then there is something fundamentally wrong with the principle on which the machine was built and with the definition which dictated that principle.

From the viewpoint of a plasterer or mason, no dry material is plastic; it must be mixed with water to develop its plasticity. Mortar or plaster is usually applied to a surface which is more or less absorbent and which sucks the water out of it. The material loses plasticity at the same rate that it loses water. Therefore, the plasticity of a material depends directly upon its ability to hold its water against the suction of the surface to which it is applied.

Visualize a trowel full of plaster applied to an absorbent wall. The layer of the plaster in direct contact with the wall will lose its water (and its plasticity) immediately. Each successive layer, counting outward from the wall, will be able to hold its water a little longer than the one under it, because the water in each layer must percolate through an increasing thickness of material in order to reach the wall. That is, the time required for the wall to suck the water out of all the plaster will depend upon the thickness of the pat of plaster. When the water has been reduced to a certain proportion, the plaster is no longer workable. Some plasters can be spread out much more thinly than others. The plasterer measures this property quite accurately by noting the number of square yards of surface that can be covered by a given volume of plaster. The more plastic the material the greater the yardage.

The rapidity with which plaster of given thickness will lose its water will depend upon the ability of the drier layers next to the wall to obstruct the passage through them of the water

coming from the outer layers; that is, upon the inherent ability of the material to retain its water. Thus the yardage is a measure of that factor of plasticity which was noted in the preceding paragraph. This factor has sometimes been considered as all important, and plasticity has been defined as being the ability to retain water against suction.[4]

Another factor which must be considered is the amount of work required to spread the plaster. Some plasters are notoriously sticky, while some work freely and smoothly under the trowel. This factor has sometimes been considered the most important, resulting in the definition that "that material is the most plastic which can be spread with the least work." [5]

Our definition, therefore, must contain two parts, as follows: (1) That material is the more plastic which has the greater ability to retain its water against the suction of the surface to which it is applied; (2) that material is the more plastic which requires the less work to spread it. A correlation of these two factors will be attempted later.

Plastic materials may be distinguished among themselves according to their working qualities. This leads to a new and more limited definition of plasticity, in that a plastic material is one which works freely and easily under the trowel and has marked ability to hold its water. In distinction to this, there are sticky materials which hold their water, but pull and work "rubbery" under the trowel, and sandy materials which work harshly and dry out quickly. This gradation of plasticity—sticky, plastic, sandy—is the one generally accepted in the trade.

## III. HISTORY OF PREVIOUS WORK

Work on the development of a means of measuring plasticity was started by this Bureau in 1909, and has been continued more or less steadily ever since. Altogether some 20 different instruments have been designed, built, experimented with, and eventually scrapped, each instrument representing one more step in our knowledge of the subject.

In the present state of general knowledge it is not difficult to build a machine and say that it will measure plasticity. The difficulty lies in offering convincing and acceptable proof that the

[4] Emley, Practical Method for Comparing the Working Qualities of Hydrates, Trans. Nat. Lime Mfrs. Assn., 1915.

[5] Emley, Measurement of Plasticity, Trans. Nat. Lime Mfrs. Assn., 1917.

machine will fulfill the claims made for it. For this reason it is thought advisable to go into the past history of the work, leading the reader up through successive failures, pointing out the sources of error in each case, and finally establishing in his mind the conviction that the present instrument will really measure plasticity.

The methods tried have been based upon seven fundamentally different principles: (1) Measurement of colloidal content; (2) measurement of viscosity; (3) compressive method; (4) range of plasticity; (5) rate of drying; (6) Carson blotter test; (7) present instrument for measuring plasticity.

### 1. MEASUREMENT OF COLLOIDAL CONTENT

Some years ago, when the chemistry of colloids first attracted attention, the theory was evolved that the plasticity of a material is directly dependent upon the proportion and kind of colloidal substance which it contains. Extended and successful efforts were made to measure the colloidal content of clays.[6] The methods employed consisted of deflocculating the colloidal matter by the addition of minute quantities of acid or alkali, or by measuring the quantity of organic dye which the colloidal matter could absorb.

Under Mr. Ashley's personal supervision, these same methods were applied to lime, but without success. The lime itself is so strongly alkaline in character that it was found impossible to deflocculate it with any reagent. The dye found most satisfactory for clays—malachite green—is an oxalate. It entered into chemical reaction with the lime and was immediately and completely decolorized. Some eighty other dyes were tried, but none was found which gave any assurance that the quantity of color removed by the lime was due to absorption and not to chemical combination.

If we concede that colloidal matter is merely matter in an extremely fine state of division, and agree that the finer the size of the individual particles the greater will be the area of their surfaces per unit of volume, then the measurement of the so-called "surface factor" becomes in effect a measure of the colloidal content. This surface factor theory is that the plasticity of a material is dependent upon the area of the surfaces of the grains. The sizes of the grains are determined as far as possible by sieves, and the finest particles are graded by elutriation.

[6] Ashley, H. E., The Technical Control of the Colloidal Matter of Clays, B. S. Technologic Paper No. 23; 1912.

Unfortunately, this method is also inapplicable to hydrates. The grains are mostly so small that even the finest sieve is not of much use in separating them. Elutriation, which depends upon the carrying capacity of streams of water of different velocities, did not give definite results because of the solubility of the lime in the water.

It is well known that the plasticity of a lime changes quite rapidly when the lime is soaked with water. If the colloidal theory is correct, then this change in plasticity should be accompanied by a change in the size of the grains. It was therefore decided that there are too many difficulties in the way to permit measuring the sizes of these very small grains when the sizes are changing continuously and rapidly.

As a summary of our experiments with this method, it may be stated that the plasticity of lime may be, and probably is, dependent upon the sizes of grains, but the experimental difficulties in measuring these sizes have to date been insurmountable.

## 2. MEASUREMENT OF VISCOSITY

It is generally accepted that a plastic material is composed of inert solid particles suspended in a liquid medium. The viscosity of the liquid should determine the freedom with which the solid particles can move, and should therefore influence the plasticity of the mass.

On this assumption it was decided to investigate the viscosities of lime pastes. For this purpose it was first attempted to use a modification of the apparatus used by Arndt for measuring viscosities of melted silicates.[7] The instrument is illustrated by the accompanying drawing (Fig. 1). A plunger of known dimensions is immersed in the liquid, and then pulled out by the falling of a known weight. The viscosity is proportional to the time required to pull the plunger out of the liquid.[8] The instrument was found to be applicable only through a very limited range of viscosities. When the weight operating the plunger was set for thick pastes, it pulled the plunger out of thin pastes so rapidly that the time could not be measured with sufficient accuracy. The dimensions of the instrument were purely empirical; it was impossible to translate the results into absolute units. Hence, when the plunger

[7] Doelter and Sirk, Determination of Absolute Values of Viscosities of Melted Silicates, Monatshefte für Chemie, pp. 49 and 611, 1911.

[8] Emley, Tests of Commercial Limes, Trans. Nat. Lime Mfrs. Assn., 1911.

or the weight was changed, the results immediately became incomparable.

While the plunger viscosimeter was in use, a new instrument, based on an entirely different principle, was being designed. This instrument rotated a plunger or paddle immersed in the liquid, and measured the force required to turn it at a constant

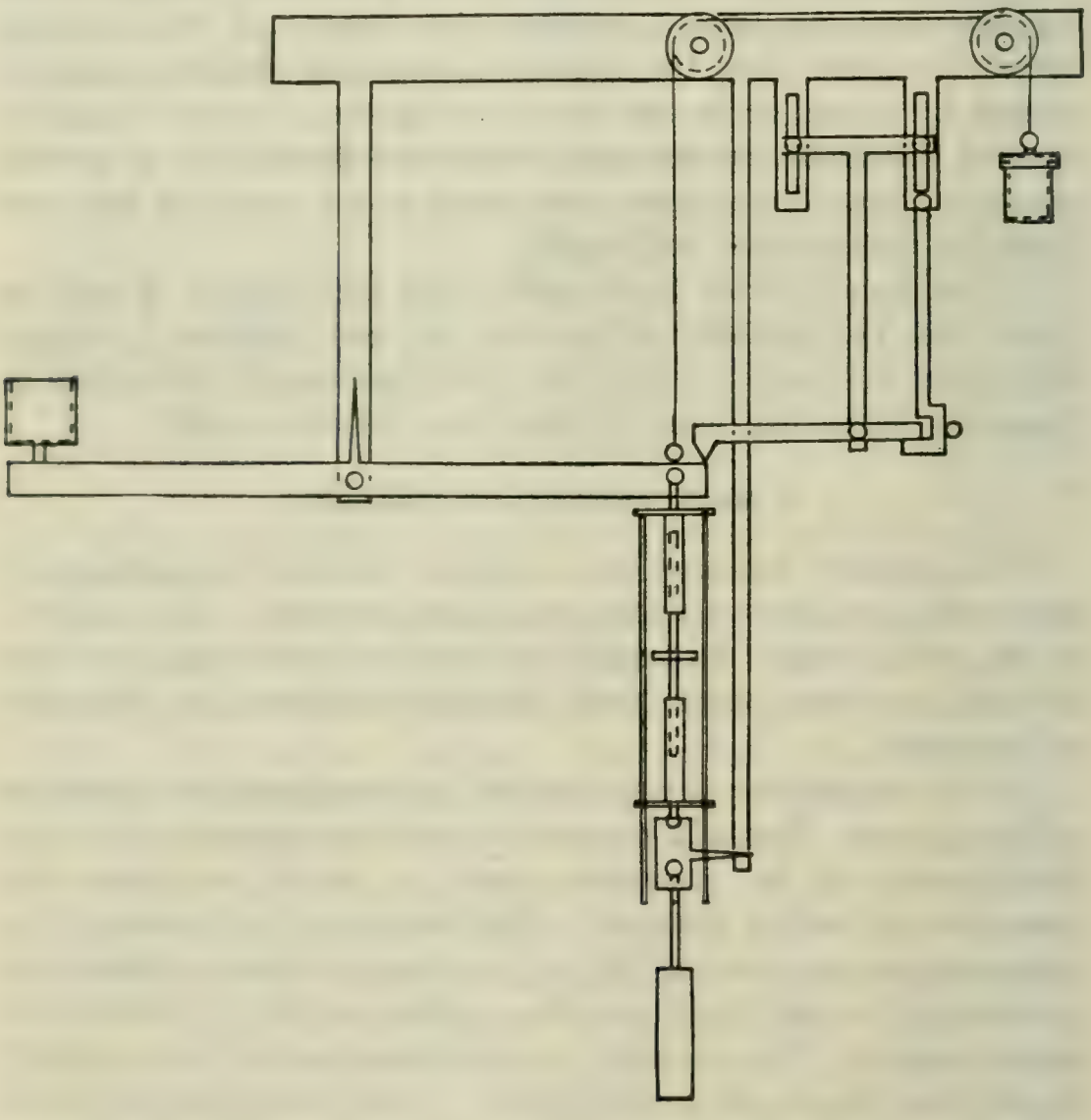

FIG. 1.—*Plunger viscosimeter*

speed. Its final design is indicated by the accompanying drawing (Fig. 2).[9] Great credit is due to Mr. Clark, the designer of this instrument, for the ingenuity with which he was able to overcome all of the difficulties previously encountered. In order to reduce friction to an absolute minimum, the paddle was mounted on jewel bearings. The necessity of mechanism to

[9] Emley, The Clark Viscosimeter, Trans. Amer. Ceram. Soc.; 1913.

turn the paddle was eliminated by using a magnetic drive. Even the friction of a speed indicator was done away with, the speed being measured by optical illusion. This instrument provided means whereby the viscosities of lime pastes could be measured throughout their entire range from thin to thick. The results could be compared to the viscosity of water as a standard, or could be calculated in absolute cgs units.

Both the plunger and the Clark viscosimeters were used for some time, making slight changes in the design. Five different shapes of plungers were tried on the former. The Clark instrument was entirely rebuilt once, and was provided with two shapes of paddles.[10]

From these numerous experiments, it was finally concluded that, while the viscosity of the liquid medium may influence the plasticity of the mass, it is not the governing factor. It is quite possible, by properly proportioning the lime and water, to produce, from any two limes, pastes having the same viscosity. Any plasterer will confirm the statement that the plasticity is dependent upon the quality of the lime, rather than upon the quantity of water.

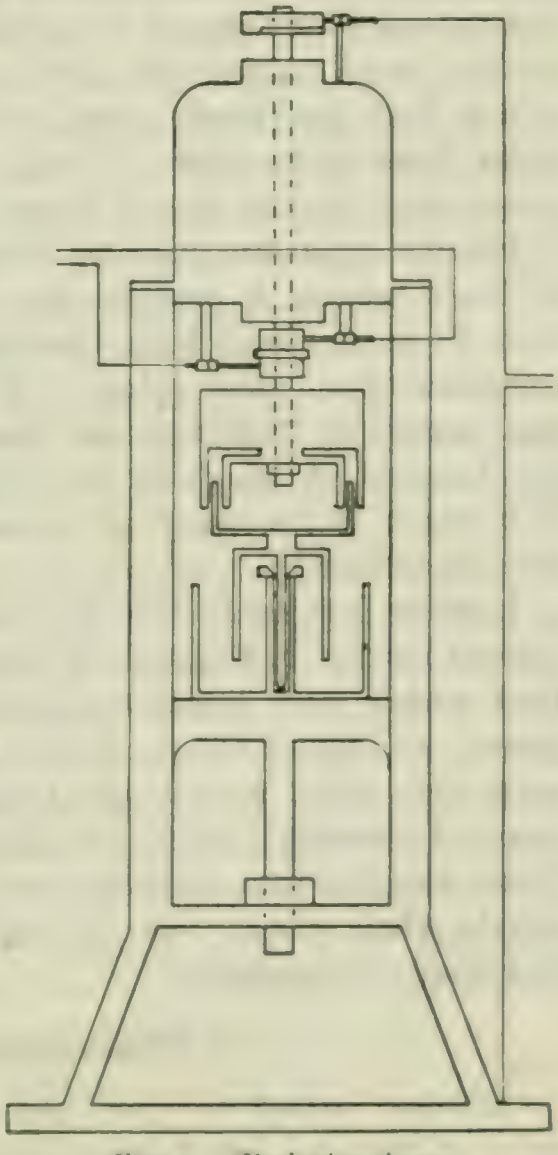

FIG. 2 —*Clark viscosimeter*

Of course, some exception may be taken to the conclusions reached, because the viscosity was not measured in the usual manner—the rate of flow through a capillary tube. Obviously it is impossible to force lime pastes, which contain large particles, to flow through capillary tubes. They can be made to flow through tubes of measurable dimensions, and this method has

[10] Emley, Effect of Consistency and Amount of Sand on the Properties of Lime Mortars, Trans. Amer. Ceram. Soc.; 1914

[11] Bleininger and Ross, Flow of Clays Under Pressure, Trans. Amer. Ceram. Soc.; 1914.

been used on clays[11] and limes.[12] However, even by this method, no definite relation has been shown to exist between viscosity and plasticity.

More recent work on this line indicates that a plastic solid differs from a viscous liquid in that the solid is able to sustain a slight initial force before it begins to deform, but after deformation has begun, the solid behaves in the same manner as the liquid—the rate of flow through a capillary tube is directly proportional to the force causing the flow.[13] This brings in another factor which had previously been overlooked. Plastic bodies may differ from each other not only in their viscosities, but in the magnitudes of the initial forces required to start deformation. While the apparatus used by Bingham and Green is inapplicable to limes because it involves flow through a capillary, it is noted that Bleininger and Ross observed this same phenomenon, the existence of a "yield value." Probably measurements made by the method of Bleininger and Ross and interpreted according to the formula of Bingham and Green would supply the missing link which is necessary to connect the viscosity of lime paste with its plasticity.

It seems inevitably true that the viscosity of a lime paste will depend chiefly on the ratio of lime to water. When this ratio is held within such limits that the paste is workable under the trowel, we know from experience that plasticity is not dependent upon this ratio, to any great extent. Therefore the measurement of viscosity, while it would indicate the magnitude of one factor entering into plasticity, could certainly not be expected to tell the whole story. For this reason the measurement of viscosity was finally abandoned.

### 3. COMPRESSIVE METHOD

Our next attack on the subject was started from the viewpoint of the engineer, dealing with plastic solids. In Merriman's text book on the Mechanics of Materials, page 378, the statement is made that when a plastic body is subjected to increasing compressive loads it will first deform and eventually rupture. The rupture will occur along a certain well-defined plane. The angle which this plane makes with the vertical is a characteristic of the material, and, when considered together with the load

[12] Lazell, E., Private communication.

[13] Bingham and Green, Paint, a Plastic Material and not a Viscous Liquid, Proc. Am. Soc. Test. Mat.: 1919.

required to cause rupture, affords a definite and reliable means for distinguishing between plastic bodies. The theory has been worked out mathematically to produce two formulas:

$$N = \cot 2\theta$$
$$S_0 = \frac{S \tan \theta}{2N}$$

$\theta$ is the angle which the plane of rupture makes with the vertical, and $S$ is the load per unit of area required to cause rupture. These formulas enable us to calculate two inherent properties of a plastic material: $N$ is the "coefficient of internal friction," and $S_0$ is the "unit cohesive strength." Translating these terms into ordinary usage, when $N$ is high, the material is sticky; when $N$ is low, the material is sandy; when $S_0$ is low, the material is short working. The conditions for maximum plasticity are an intermediate value for $N$ and the highest possible value of $S_0$.

An instrument was built to measure the compressive strength of green lime pastes and mortars. It is shown in the photograph, Fig. 3. It operates on the same principle as an Olsen testing machine on a very small scale.

A great many experiments were made with this instrument, the results being published in three papers.[14] It was found that the method does give valuable information about the plasticity of lime, but, like the measurement of viscosity, it does not tell the whole story. The question of consistency again looms up like an insurmountable obstacle. With a very thick paste, $S$ is large and $\theta$ is nearly zero. As the paste is thinned down by the addition of water, $S$ decreases and $\theta$ increases, until, when the body changes from a plastic solid to a viscous liquid, $S$ becomes equal to zero and $\theta$ to 45°. In other words, the plasticity of a material, when measured by this method, depends upon the ratio of lime to water, which is not true. The method was therefore abandoned.

#### 4. RANGE OF PLASTICITY

The experiments with the compressive method emphasized the previously known fact that plastic materials vary in the length of their plastic range. If increasing amounts of water are added to hydrated lime, the changes in consistency will occur in the following order: dry powder, damp powder, sticky

[14] Emley, Deformation of Plastic Bodies Under Compression as a Measure of Plasticity, Trans. Amer. Ceram. Soc., 1915. Measurement of Plasticity of Hydrated Lime by the Compression Method, Trans. Nat. Lime Mfrs. Assn., 1916. Compressive Method of Measuring Plasticity, Trans. Nat. Lime Mfrs. Assn., 1916.

mass which when molded is practically a solid, plastic material, liquid. Suppose a given hydrate changes from a solid to a plastic material when mixed in the proportion, 80 per cent lime, 20 per cent water. When the proportion is 50 per cent lime, 50 per cent water, the material changes from a plastic material to a liquid. Then the "plastic range" of this lime is $80-50=30$ per cent. It has been found by experience that, as a general rule, the more plastic the material the greater will be this range. This method has been employed for many years in the study of clays, under the title of the "Atterberg Plasticity Method."[15] The compressive method described above provided quite accurate means for determining the end points of the plastic range, and the results obtained from experiments with the compressive method could be used as data for the comparison of plastic ranges.

From a study of these data the following conclusions were drawn: (1) Limes as a class follow the general rule, the more plastic the lime the greater the range. (2) The end-points can not be determined with sufficient accuracy to permit differentiation between similar limes. Differences which are quite noticeable under the trowel can hardly be detected by this method. (3) The method is entirely inapplicable and misleading when it is used as a basis of comparison for dissimilar substances, such, for instance, as neat lime and lime mortar. This last conclusion, which really eliminates further consideration of the method, has been verified by other investigators.[16]

### 5. RATE OF DRYING

The quantity of water which must be mixed with a lime to render it plastic is conceivably a function of the size of grain of the lime and is to that extent a measure of its colloidal content. If plasticity depends upon the presence of colloidal matter, then the quantity of water required should be at least in some degree a measure of plasticity. This would probably be true if it were not for two factors: (1) The quantity of water is not definite for any given material; there is a range in the proportions of lime and water within which all mixtures are plastic. (2) Plasticity is not only quantitative, but also qualitative in its nature. It is impossible, by the mere addition of water, to bring all limes to the same degree of plasticity.

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[15] Albert Atterberg, International Reports on Pedology; 1911.

[16] C. S. Kinnison, Study of the Atterberg Plasticity Method, Trans. Amer. Ceram. Soc.; 1914.

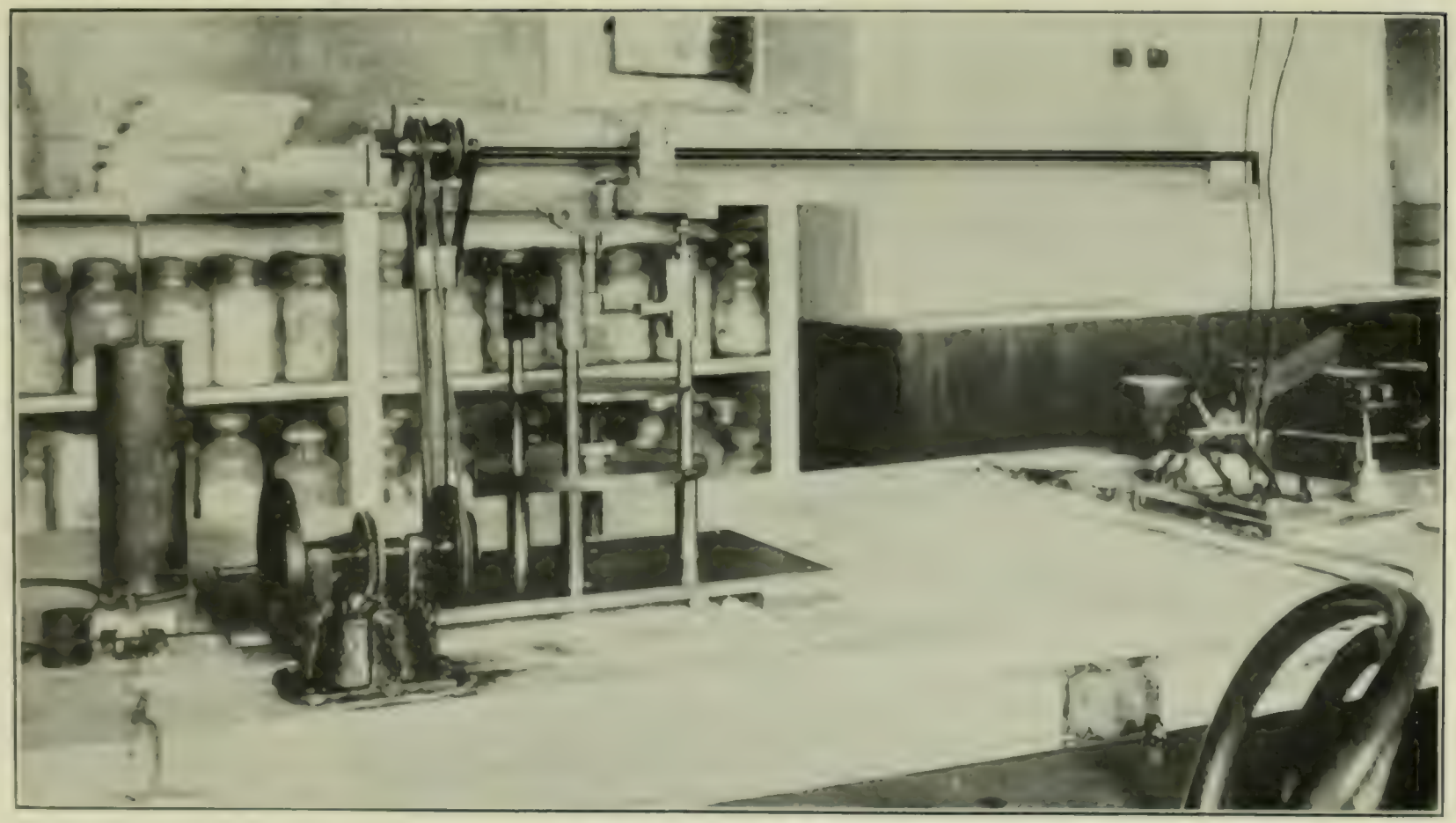

FIG. 3.—*Compressive machine*

Plasters are used by spreading them on absorbent surfaces. They must be mixed with enough water to make them plastic, and they must be able to retain that water against the suction of the surfaces on which they are spread. The length of time during which a plaster can hold enough water to maintain its plasticity will depend not only on the quantity of water originally present, but also on some inherent property of the plaster which gives it the ability to retain water.

An attempt was made to measure this property of hydrates. Pats of lime paste were spread on plaster blocks. The blocks sucked the water out of the lime. The rate of drying was measured by sticking a needle into the paste every few seconds. The method was found to give very promising results.[17] It was refined to some extent by molding the lime paste in the form of a wedge, so that the rate of drying could be followed up the wedge, and the thickness of the dried paste could be plotted against the time.[18]

From the reasoning given above, it will be understood that this method was not intended to measure plasticity. It measures the ability of the material to retain its water, which is only one of the factors governing plasticity. The method performed very much better than was expected; it differentiated sharply between Ohio finishing hydrates and nonplastic hydrates. This is taken to mean that the rate of drying is a measure of the most important factor governing plasticity. So predominant is the influence of this factor that the method forms a reliable basis for the comparison of different classes of materials

The ability to retain water, while the most important, is not the only factor governing plasticity. The measure of this ability permits distinction between classes of materials, but the other factors must be considered when attempting to compare materials in the same class.

### 6. CARSON BLOTTER TEST

During an informal discussion at the 1916 meeting of the National Lime Manufacturers' Association, Mr. W. E. Carson, who was then president, described a test which he had found satisfactory for the measurement of plasticity. This is essentially a duplication on a small scale of the action of a plasterer when spreading plaster on a wall. The wall is represented by a sheet

[17] Emley, Practical Method for Comparing the Working Qualities of Hydrates, Trans. Nat. Lime Mfrs. Assn.; 1915.

[18] Kirkpatrick, F. A., Circular Letter to Members of Committee C-7, Am. Soc. Test. Mat.; 1913.

specimen makes one revolution in 6½ minutes, and moves upward one-thirteenth of an inch in the same length of time. The upward motion presses the surface of the specimen against the disk. This disk is conical in form, mounted point downward on a vertical shaft. It is free to turn, but can not move upward. This conical disk is supposed to represent the trowel. Its sides make an angle of 10° with the horizontal, this being assumed to be about the angle that a plasterer's trowel makes with the wall. While the disk is free to turn, each increment of rotary motion requires an increasingly larger force to accomplish it. A cord connects the shaft of the disk to a pulley, to which a pendulum arm is rigidly attached. As the disk turns it winds up the cord, pulls the pendulum more and more away from the vertical and toward the horizontal, and thereby continuously increases the force required to produce further motion. The pendulum carries a pointer which moves over a circular scale, so that at any time the angle which it makes with the vertical can be read. The force which is being exerted to turn the disk is directly proportional to the sine of this angle. The force is also directly proportional to the weight of the pendulum; the magnitude of the scale readings can be changed by using bobs of different weights attached to the pendulum. Two bobs are provided, weighing 350 and 800 grams, respectively.

The upward spiral motion of the specimen against the disk results in a twisting moment, which tends to spread the specimen out on the plaster block. The pendulum provides means of measuring that part of the force exerted which is acting parallel to the surface of the specimen. The absorption of the plaster block gradually removes water from the specimen and permits measurement of the rate of drying.

From the drawing and photograph, it will be noted that three changes have been made in the instrument since it was built: (1) It was originally intended to permit the disk to move upward, and to measure the force required to cause motion in this direction. A large number of experiments with the first edition of the instrument demonstrated conclusively that the magnitude of this force is not interesting. This mechanism has therefore been locked so that it will not work, and it may well be omitted from further designs. (2) The design calls for a flat disk as well as a conical one. A large number of experiments were run with this flat disk, but it was found that the conical one is more satis-

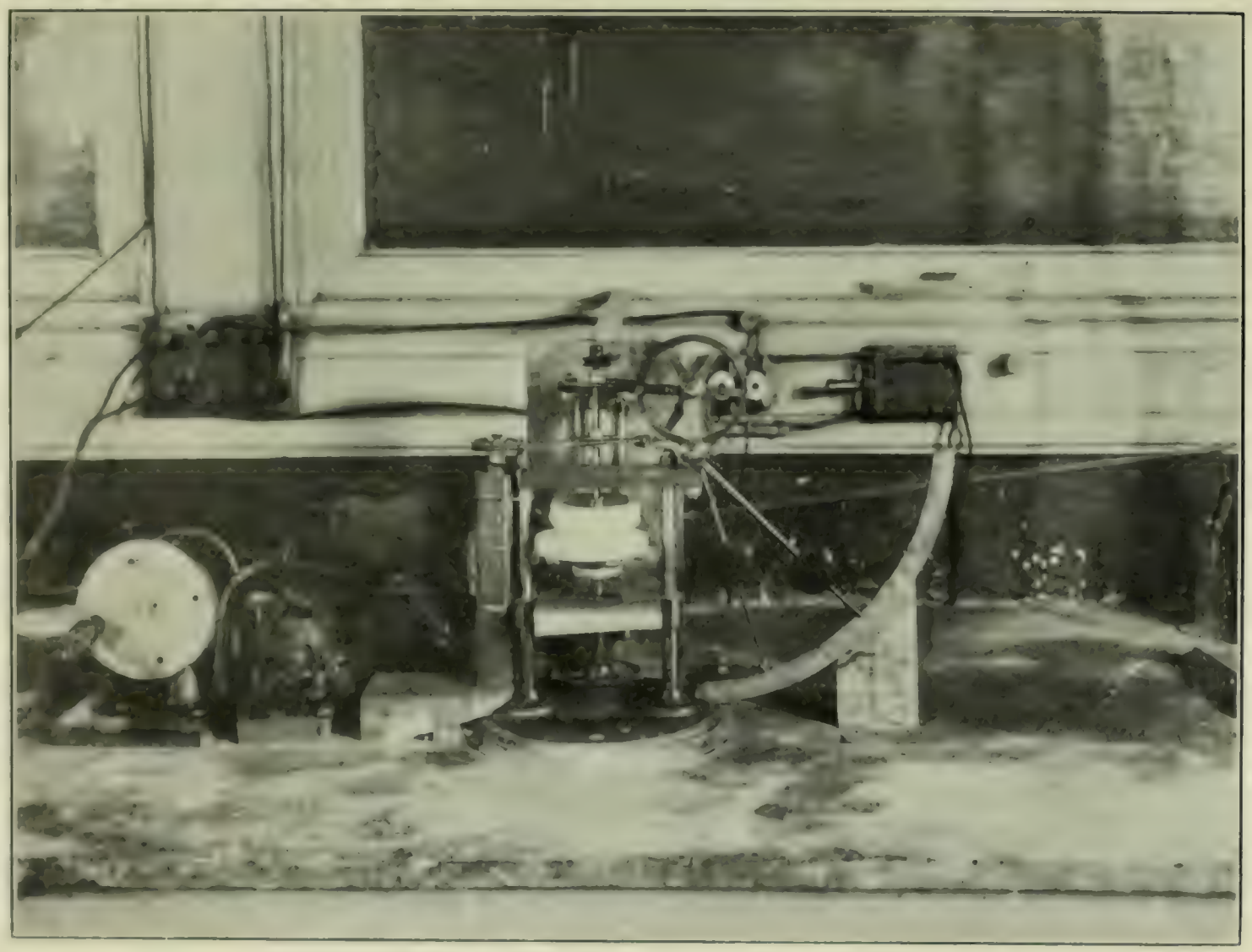

FIG. 4.—*Plasticimeter, original design*

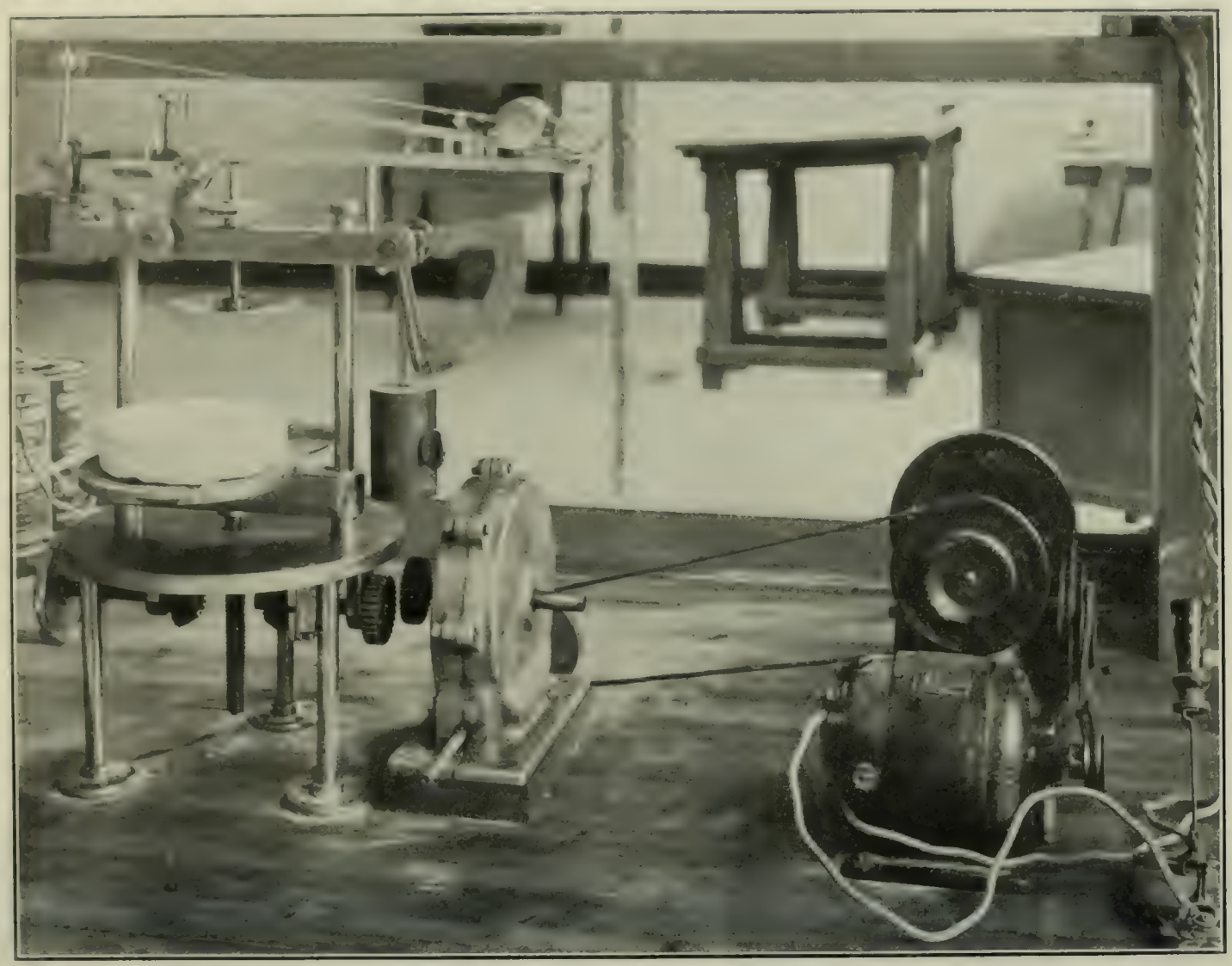

FIG. 5.—*Plasticimeter, present design*

factory for plasters and mortars, though the former may possibly give some valuable information about clays. (3) The original design calls for a speed of 3 rpm. This was found to be much too fast for plasters, and the speed now in use—one revolution in 6½ minutes—has been finally adopted as satisfactory. It may be found necessary to increase this speed when dealing with materials which set very quickly (unretarded calcined gypsum, for instance), but determinations made at different speeds are not comparable.

### 2. METHOD OF RECORDING RESULTS

While the instrument is in operation, the specimen is continuously drying out. This, together with the continuously increasing area of contact between the specimen and the conical surface of the disk, results in a continual increase in the force tending to turn the disk. The pendulum gradually swings out over its circular scale. The results of an experiment are expressed as the relation between time and force. The time is counted in minutes, beginning with the time when the first lot of the specimen was put into the mold. Since one bob only is used during any experiment, the force is recorded as the sine of the angle which the pendulum makes with the vertical. It is convenient to express the results in the form of a curve, using time as the abscissa and force as the ordinate. A large number of experiments, conducted during a period of three years, have enabled us to recognize the typical curves of plastic and nonplastic hydrates. The former will start to rise late and will continue to rise gradually. The latter will start to rise early and will continue to rise abruptly. The shape and position of this curve constitute criteria of plasticity which all of our experiments have shown to be infallible.

### 3. INTERPRETATION OF RESULTS

If, for example, one is conducting experiments to improve the plasticity of a material, each change in the manufacturing process can be followed up by the instrument and the curve obtained can be filed away for future reference. This ability to refer back to previous results is of great practical importance. Herein lies the great advantage of the instrument over the Carson blotter test.

The use of a curve to express results, has, however, many disadvantages. It requires some little study of a curve to deduce its exact meaning, and its use is therefore inconvenient. While

the comparison of two curves usually enables us to tell without doubt which lime is the more plastic, the relative degrees of plasticity are still indeterminate. An attempt has been made to draw an arbitrary line across the curve sheet and state that when a curve lies to the right and below this line the hydrate can be used as a finishing lime; when a curve lies to the left and above the line, the hydrate is nonplastic. This attempt has thus far been entirely successful, but there is always the possibility of a quibble about the position of the arbitrary line. If one curve crosses another in two places, as frequently happens with similar materials, it is impossible to tell from the curves which of the two substances is the more plastic.

For these reasons, many attempts have been made to find numerical expressions for the curves. It must be emphasized that these attempts are merely for the sake of greater convenience, and that the curves remain as the final criteria.

#### 4. NUMERICAL EXPRESSION OF RESULTS

It will be remembered that the speed of the machine is constant. The abscissa representing time can, therefore, by a suitable change in the scale, be made to represent distance. The area under the curve then becomes the product of the force and the distance through which it acts, which, by definition, is the work done. If we accept the old statement that that lime is the most plastic which can be spread on the wall with the least work, then the area under the curve is a direct measure of plasticity—the less the area the more plastic the material.

Unfortunately, this area could not be directly measured. There was no right-hand end to the curve, no stopping place. The force continued to increase with the time indefinitely. An attempt was made to remedy this defect by setting an arbitrary time limit. The work done during the first five minutes was established as a basis for comparison.[20] The results were extremely gratifying, so much so that this method was on the point of being adopted as standard. Further study of it, however, brought to light two serious fallacies: (1) In a majority of cases the curve could not be continued for five minutes. Either the specimen ruptured or else the force ran off the scale. It was necessary, therefore, to extrapolate the curve in order to measure its area for five minutes. This is of doubtful expedience in any

[20] Kirkpatrick and Orange, Tests of Clays and Limes by the Bureau of Standards Plasticimeter, Jour. Amer. Ceram. Soc., March, 1918.

case, and in cases where the specimen ruptured it is positively wrong. (2) It requires very little work to spread pure sand, if the operation can be completed before the sand has dried out. This method would therefore show sand to be one of the most plastic materials, which of course is absurd. The trouble here is not with the method, but with the definition. That material which can be spread with the least work is not necessarily the most plastic. The thinness to which the material can be spread, the time during which it can be worked, its ability to retain water (all of which terms are synonymous), is a more important factor in plasticity than is the quantity of work done on the material. While it requires less work to spread sand than lime, the sand dries out so quickly that it can not be spread to the same thinness nor worked for the same length of time and is therefore less plastic.

It is absolutely necessary, therefore, to find a right-hand end to the curve, not an arbitrary one, but one which depends upon the inherent character of the material. This has been accomplished with the second edition of the instrument. By using a slower speed and a heavier bob, it has been found possible to reach the point of rupture of every specimen thus far examined. The force does not continue to increase with the time indefinitely. A point is eventually reached where, due to the largeness of the force and the dryness of the material, the specimen breaks. This break is plainly visible, and is indicated in the results as the point where the curve abruptly ceases to rise.

Having now a definite end point to the curve, it is a simple matter to compare the quantities of work which these curves represent. Here again the argument leads to absurdity. The work done on sand is very much less than the work done on lime, yet the lime is more plastic.

Reverting back to the preceding discussion, it will be remembered that plasticity is dependent upon two factors, the time during which the material can be worked and the work required to spread it during that time. Of the two the former is the more important. By considering only the area of the curve we have neglected the first and more important factor. Mathematically it can be stated that plasticity varies directly as the time and inversely as the work. The work, however, is represented by the area, force multiplied by time. A combination of these two statements would indicate that $P = K\frac{T}{F \cdot T} = \frac{K}{F}$, or the plasticity varies

inversely as the force and the time element is completely eliminated. This, again, is absurd. The trouble is that our mathematics have given equal values to time and work, whereas we know that the former is more important and should carry more weight than the latter. The $T$ in the denominator should not be able to cancel completely the $T$ in the numerator.

### 5. ADOPTED METHOD OF EXPRESSING RESULTS

We have not been able to determine the relative importance of time and work. We have been able to establish the fact that the former is of far greater importance than the latter—is, in fact, the predominating factor. If we consider two plasters, one of which can be worked on the wall for 30 minutes and the other for

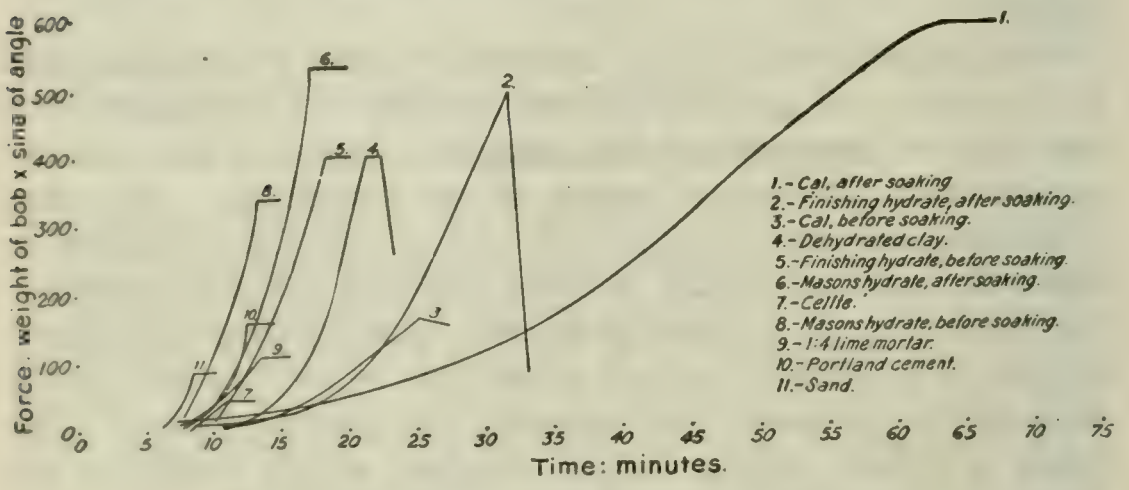


FIG. 6.—*Plasticity curves of miscellaneous materials*

only 15 minutes, there is no doubt that the former would be generally accepted as the more plastic, regardless of the relative quantities of work required to spread the two. If, on the other hand, two plasters can be worked for exactly the same length of time, then that is the more plastic which requires the less work to spread it.

Acting on this theory, plasters have been divided into classes according to the length of time during which they can be worked, and the plasters within each class have been ranked according to the work required to spread them.

As a matter of convenience, 5-minute intervals have been fixed as a basis of classification. The curves of some miscellaneous materials are shown in Fig. 6, and the results are classified in the table given below.

## V. PLASTICITIES OF MISCELLANEOUS MATERIALS

The following table calls attention to certain facts. Before soaking, the finishing hydrate is not much better than the nonplastic. Soaking raises the finishing hydrate three classes, the nonplastic hydrate only one class. Materials in the 20-minute class or better can be used as finishing plasters, those below the 20-minute class can not.

**TABLE 1.—Relative Plasticities of Miscellaneous Materials**

| Class | Relative force required to spread | Material | Class | Relative force required to spread | Material |
|---|---|---|---|---|---|
| 30-minute | 14 | "Cal"[a] soaked overnight | 10-minute | 12 | Celite |
| | 51 | Finishing hydrate, soaked overnight | | 13 | Nonplastic hydrate, not soaked |
| 25-minute | 20 | "Cal" not soaked | | 15 | 1 : 4 lime mortar |
| 20-minute | 37 | Dehydrated clay | | 16 | Cement No. 1 |
| 15-minute | 24 | Finishing hydrate, not soaked | | 16 | Cement No. 2 |
| | 34 | Nonplastic hydrate, soaked overnight | 5-minute | 3 | Cement No. 3 |
| | | | | 5 | Very fine sand |

[a] "Cal" is a proprietary material which is intended to be added to concrete to accelerate its early hardening.

EXPERIMENTAL EVIDENCE.—"The proof of the pudding is in the eating." The principle upon which the plasticimeter operates appears to be fundamentally sound, but if the results obtained by its use are erroneous, the theory will not be able to hold its own against the facts. On the other hand, criticism of the theory must be expected; but, if it is shown that the results obtained are correct, this will afford the best possible means of substantiating the theory.

In order to prove that the instrument does give correct results, experiments have been conducted along two different lines—a determination of the effect of consistency upon the plasticity of lime pastes and a determination of the effect of the quantity of sand on the plasticity of lime mortars.

## VI. EFFECT OF CONSISTENCY UPON PLASTICITY

It was noted above that consistency has little influence on plasticity. If a lime paste is not plastic, no amount of water which may be added to it can render it so. The converse of this is also true; a plastic lime remains plastic, regardless of the quantity of water which may be added to it. Of course, these

statements are true only when the material is really plastic—when it does not approach too closely to either the solid or liquid conditions. Any plasterer will verify these statements, and they can be corroborated with a trowel at any time.

The consistency does, however, have some influence. Obviously, the time required to dry the water out of a plaster, while it depends chiefly on the ability of the plaster to retain water, must be somewhat dependent upon the quantity of water originally present. Experience shows that a wet paste will have somewhat, though very little, better spreading qualities, than a drier one made of the same material.

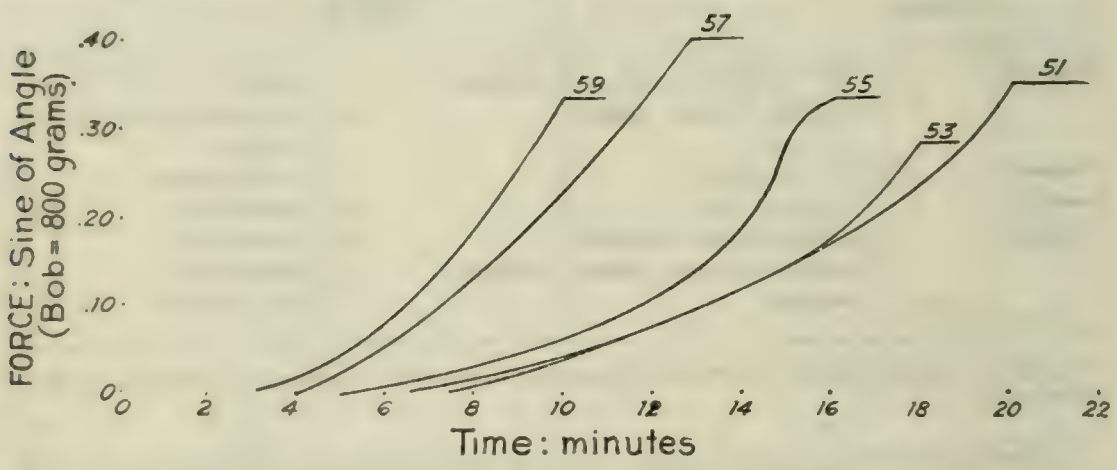


FIG. 7.—*Effect of consistency on plasticity*

To illustrate this effect, and at the same time obtain some idea of its magnitude, a series of specimens were tested, all made of the same lime, but with different proportions of water. The results are shown by the curves, Fig. 7, and are tabulated as follows:

**TABLE 2.—Effect of Consistency Upon Plasticity**

| Per cent lime | Per cent water | Class | Force | Per cent lime | Per cent water | Class | Force |
|---|---|---|---|---|---|---|---|
| 51 | 49 | 20-minute | 34 | 57 | 43 | 10-minute | 23 |
| 53 | 47 | 15-minute | 14 | 59 | 41 | 10-minute | 33 |
| 55 | 45 | 15-minute | 28 | | | | |

Evidently, the wetter the consistency the more plastic the material. In practice the consistency must be at least dry enough so that the plaster will not run off the trowel. The wettest specimen included in the above series is possibly a little wetter than could be readily handled. It is impracticable, therefore, to make from this hydrate a paste which would have the same plasticity as that shown by the finishing lime in Fig. 6.

The instrument corroborates our experience as to the effect of consistency in every respect.

Consistency is not of very great importance. Changes due to consistency can practically never be of sufficient magnitude to render a nonplastic hydrate plastic or the reverse. For this reason consistency as judged by the eye will usually be close enough for practical purposes.

In cases where greater accuracy is desired, as when comparing similar hydrates, the consistency must be considered and accurately measured. We have found it convenient to use the Southard vicosimeter [22] for this purpose. This is a modification of the "slump test" which has been in general use on concrete for some time. The molded cylinder is 2 inches in diameter by 2½ inches high. A sample of plaster gaged ready to put on a wall was tested and found to slump one-half inch; that is, when the cylinder of paste was removed from the mold, it deformed of its own weight until it was only 2 inches high. This was taken as the "normal consistency." In all plasticity experiments the material being examined is mixed with enough water so that it will show a slump of one-half inch when tested in the Southard viscosimeter.

## VII. EFFECT OF PROPORTION OF SAND UPON PLASTICITY

The quantity of sand which is added to a lime paste to make a plaster is governed almost entirely by the plasticity. The mortar mixer adds as much sand as he can without making the mortar so lean that it can not be worked successfully.

It is usually claimed, but never conceded, that a dolomitic hydrate will carry more sand than a high-calcium hydrate. Certainly the dolomitic hydrate has the advantage of greater plasticity in the neat paste. As hydrate is replaced by successively larger amounts of sand the mixtures become leaner. Their plasticities approach each other and finally become equal when all of the hydrate has been replaced by sand. Since the plasticity of the sand is lower than that of the lime, it is evident that the replacement of lime by sand will cause a continuous decrease of plasticity. At a certain point it will be found that the plasticity of the mixture is so poor that it can no longer be used for the purpose intended. This point indicates the sand-carrying capacity of the lime. It is obvious that, in order to measure the sand-carrying capacities of different limes, it is essential that the sand

[22] Report of Committee C-11, Am. Soc. Test. Mat., 1919.

be uniform for all tests. A standard sand, to be used in testing plastering materials, is a necessity. It is worth noting that the process can be reversed, and, by the adoption of a standard lime, can be used to measure the lime-carrying capacity of different sands.

Probably the sand-carrying capacity will be found to vary with the purpose for which the material is to be used. It was noted above that a lime must be in the 20-minute class or, better, to be used for finishing. Possibly a 15-minute mixture of lime and sand

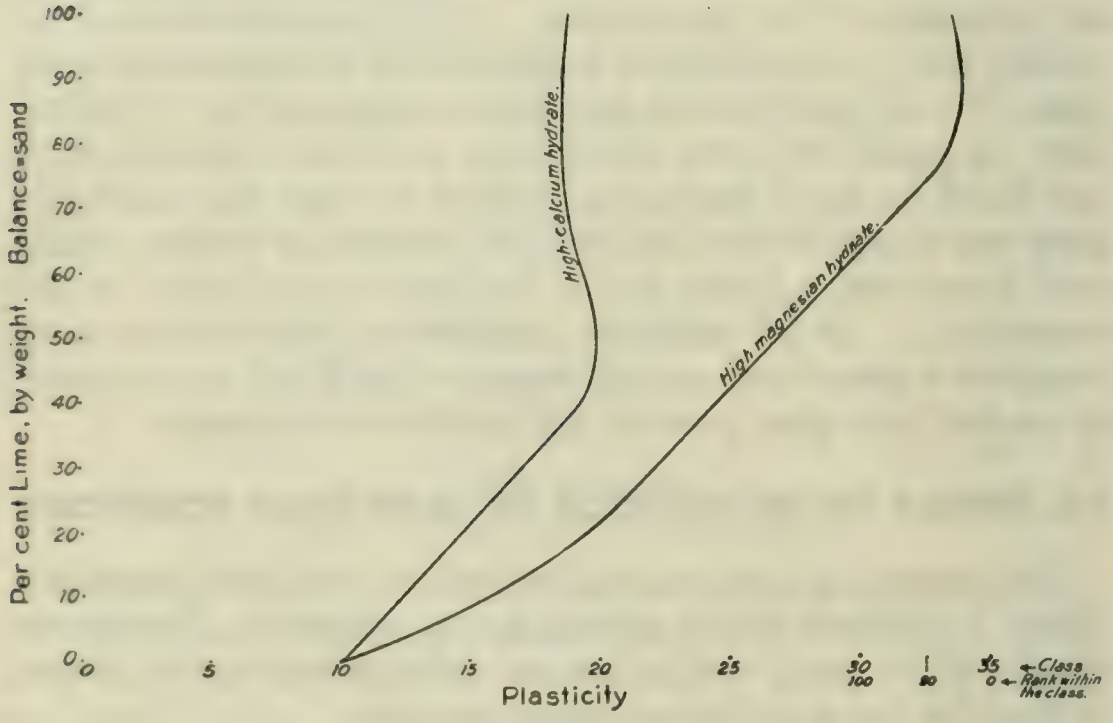


FIG. 8.—*Effect of proportion of sand on plasticity*

will be satisfactory as a scratch coat on metal lath, while for brown coat we may be able to go still leaner, to the 10-minute class.

Fig. 8 shows the plasticities of all proportions of lime and sand. It offers definite proof that the dolomitic hydrate does carry more sand than the high-calcium hydrate. It shows that a mortar made of dolomitic hydrate is more plastic than one made of high-calcium hydrate, regardless of the proportion of sand, up to that point where they are both so lean that there is little difference between them. It shows that the addition of a small amount of sand to a high-calcium hydrate slightly improves its plasticity, a fact which is frequently taken advantage of in practice.

## VIII. CONCLUSION

An instrument has been devised that will measure plasticity. We now have a tool with which to work on the important investigations into the cause of plasticity and the improvement of plasticity.

At the instigation of J. J. Earley another instrument is now being built which is much simpler in design and on a much larger scale than the present machine. It is proposed to use this new plasticimeter to attack the problem of the plasticity of concrete.

The instrument is available for use in writing standard specifications for lime and gypsum.

The investigation has been conducted during such a long period of time that it is difficult to make due acknowledgement to all whose thoughts and work have been included in the final product. Those who have contributed the most are, probably, J. J. Earley, W. E. Carson, E. E. Eakins, A. V. Bleininger, P. H. Bates, F. A. Kirkpatrick, W. B. Orange, S. K. Kaczorowski, and C. H. Bacon.

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